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TRACE MATERIALS IN WASTES DISPOSED TO COASTAL WATERS:

Fates, Mechanisms, and Ecological Guidance & Control

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Feldman, Milton H.

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16. Abstract Wastes currently being discharged to the coastal waters of the United States include Trace organic contaminants (TC), trace elements (TE), and other trace materials (TM). Those TM dealt with included: (1)known violently noxious materials (Pb^{++}, $[CN]_2^{=}$, Hg^{++}); (2) materials which are biostimulatory to some species (cobalamin, iron chelates, thiamin, biotin ,Mn, Mg; and (3) materials which are bioinhibitory for at least some species in various mechanisms (DDT, Se, Mn, Mg). A different view of the problem was taken in which ways of selecting the optimum organism to utilize a particular waste were preferred to methods of removing it conventionally. A thorough literature search revealed a significant lack of literature in waste breakdown for both qualitative and quantitative evaluation. ~~It was concluded that~~ Further studies should be performed for each known trace material to determine: (1) the mechanism whereby it is secluded; (2) the metabolic threshold; (3) the active level; (4) the harmful level; (5) the speciation requirements; (6) the absolute rates in and out of the compartments of which coastal waters, sediments, chemical system phases, and biota may be considered as composed. Evaluations such as these were performed for DDT, and they must be performed for the known set of waste constituents before rational action to prevent damage to the oceans is possible. (Lowry-Texas)

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Abstractor Mark V. Lowry

Institution Texas Univ, Austin

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TRACE MATERIALS IN WASTES DISPOSED

TO

COASTAL WATERS

Fates, Mechanisms, and Ecological Guidance and Control

by

MILTON H. FELDMAN

Chief, Chemical and Biological Oceanography Branch
National Coastal Pollution Research Program

Working Paper 78

United States Department of the Interior
Federal Water Quality Administration, Northwest Region
Pacific Northwest Water Laboratory
200 SW 35th Street
Corvallis, Oregon 97330

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INTRODUCTION AND SUMMARY

The essence of the argument implicit in this analysis might be expressed as follows:

The kinetics of bloom phenomena and the culmination biomass achieved are not the specific problem we address, nor are the gross nutrients although all these questions are certainly related and of interest. What we ask is which algae, and which benthic and pelagic, species will be "crucially" aided or hindered by the trace material ambient we can create through our waste management procedures. What specific mechanisms operating via trace guidance and control materials are available to us for species control rather than total biomass control?

We are aware of and concerned with the work of our colleagues studying eutrophication of lakes; but eutrophication levels of phosphorus and the utility of reduction of phosphorus introduced into waters from various effluents is not necessarily the problem from our oceanic point of view; nitrogen supply may well be more limiting in the ocean than phosphorus. The role of silicon at the origin of the food chain is undetermined.

If we can ensure a desirable crop propagation, then it might be wiser to give that crop all the phosphorus, nitrogen, or silicon it can beneficially use.

As an example of specific problems, we might cite the concentrating of metal atoms. It is immediately apparent that the concentration of certain metal atoms by aquatic biota, e.g., the often cited Zn^{65} in mollusca off the Columbia River, is becoming a more sophisticated problem.

Is the atom concentrated by similarity and is it laid down with chemically similar atoms as strontium or plutonium in bone, or is it like vanadium to some blood systems as iron to some others? Is the atom concentrated as an essential metabolic agent and is it then found in the liver, or is it merely an accidental ingestion with no mechanism available for excretion and is it then found in the kidney? In other words, the atom's role in the life cycle is the reason we should study it not merely to record that here is an element significantly concentrated (with possible food chain significance) or an easy to follow tracer convenient to observe.

We need to know the mechanism whereby it is secluded, the metabolic threshold, active level, and harmful level, and the speciation requirements, and absolute rates in and out of the compartments of which coastal waters, sediments, chemical system phases, and biota may be considered as composed.

It was done for DDT and it ought to be done for the set of wastes' constituents whose management is properly our problem.

I.

AVAILABLE TRACE MATERIAL DATA

Natural Processes

In studies of the chemical, geochemical, and biologically directed chemical and physical mechanisms controlling the behavior and fate of waste materials introduced into the sea, it is apparent that the controlling mechanisms are "natural," i.e., not different, but obeying the same chemical and biological laws as control the naturally introduced materials. Details of rates, concentrations, and specific materials will vary from point to point and these differences are to be understood by means of the same practices and principles as have been applied to chemical and biological oceanography (Richards, 1969).

Coastal Waters

The truly significant difference, however, is one of locale and of the specific physical, chemical, and biological mechanisms prevailing in that ambience - the near coastal waters and estuaries, the zones of rapid mixing of the world ocean waters, and the fresh waters run off from the land. Since this zone extends from well inland in some instances, to the entire sea mass in others, it represents the gamut of possibilities and, of course, of difficulties. It is possible, however, to treat the important coastal waters as a fairly well-defined area in any given case, with more or less input from neighboring waters, fresh or salt.

TM = TE + TC

It will become apparent from a consideration of the documents studied and listed in the references that our subject rapidly became trace materials (TM), both trace elements (TE) and trace organic compounds (TC) in the coastal and estuarine zones of the neritic ocean. It is not claimed that all the answers to the fate of and the influence of wastes disposed of in the coastal zones devolve into a question of TM only. But the need for detailed information on the behavior, mechanisms, and fate of TM has been apparent. Provasoli (1963), Johnston (1963, 1964), Goldberg (1965).

In a meeting at Jackson Hole, Wyoming, July 7-12, 1969, committees of various disciplines addressed to the question - the rational management of waste disposal in coastal and estuarine waters: especially the chemistry and biology panels emphasized the need for TM information, descriptive and mechanistic, but also the Committee on Monitoring listed the need for a specification of trace elements and suitable procedures for a complete monitoring system (NASCO-NAECO, 1969).

We deal with TM which

(a) are known violently noxious materials

Pb^{++}, $(CN)_2^{=}$, Hg^{++}

(b) are biostimulatory for some species

cobalamin, iron chelates, thiamin, biotin, Mn, Mg,

(c) are bioinhibitory for at least some species in various mechanisms.

DDT, Se, Mn, Mg.

Thus, cobalamin is a *catalyst*, EDTA is a solubility and concentration *control* material, Mn is an *enzyme co-factor*, and other mechanisms certainly occur. Case (a) is not included in our discussion except to refer to it as covered by Sharp (1969). But the cases (b) and (c) are the subject of our proposed Guidance and Control for ecologically useful use of wastes in the coastal environments.

We have limited our assessment to chemistry and biology, and having assumed that chemistry and biology determine ecology and ethology, have concluded they can provide possible means for guidance and control.

The words contaminant, pollutant, which here have negative connotation, are in far more popular use these days than words like recharge, useful use of nutrients, ecological guidance and control*, which have positive connotations. This is not an isolated phenomenon. A review of Roget's Thesaurus shows that there are generally more ways to describe bad situations than good, more ways to denigrate

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*The words guidance and control are words suggestive of technologically feasible ends; management of wastes in coastal waters implies legal and administrative relations.

than praise. Our language is part of how we think. Since in the case of environmental quality control the need is for positive thinking of solutions to problems, it is suggested here that "proper guidance and control" of wastes disposed of to the marine environment can result in positive contributions - good rather than deleterious effects. The only prerequisite to this desirable state of affairs is knowledge - sufficient understanding of how things work. While this point of view, that knowledge engenders good, is no longer so generally accepted as it once was, it probably is still a useful approach to technological problems.

The author, therefore, has evaluated the available information on the probable TM content of domestic wastes input to coastal waters and has considered their possible impact. As will be seen, the quantitative data on the input and its chemical, biological, and physical behavior and fate is scanty indeed, but every indication from known and suspected relations in chemical and biological oceanography is that while the impact could be most significant, it may be controllable.

Even with the considerable ecological knowledge apparently available prior to the widespread use of DDT on land to control certain insect species, it is now clear that much more basic biological, chemical, and physical information would have been desirable. We are already putting very large amounts of general municipal wastes (Parkhurst and Bargman, 1969) and specific industrial

wastes (Arnold, 1950) into the coastal waters, and even such materials as chemical warfare reagents have been subjects (numerous newspaper reports, mid-1969) for oceanic disposal. It is claimed that large scale oceanic dumping can be safely carried out without damaging the coastal and oceanic environment (Sport Fishing Institute, 1969). However, Waldichuk (1968) has listed the wide ranging needs for improved methodology in the required long-term studies. The basic knowledge to be drawn upon to enable the safe disposal claimed (Sport Fishing Institute, 1969) is not referenced and does not seem to be available at this time (November 1969), but what information is available seems to indicate that the results might be slow in eventuating but startling in their finality. Thus, consider the early optimism, based on lack of sufficient data, during an examination of the benthos in a very limited area of acid-iron waste dumping off New York City (Arnold, 1950). Compare that early optimism with the later guarded pessimism based on observed benthic depletion and diversity reduction (Sport Fishing Institute, 1969) in the same general location, but now covering a much larger area. Given the sediment scouring and washback to the Long Island beaches, we see the need for prior study and conservative extrapolation. Incidentally, the sediment scouring and washback to the beaches of Long Island could have been predicted from known long-term phenomena (Trask, 1955) for that well-known neritic system.

At the same time as these oceanic questions are raised, the Congress is reviewing and passing legislation designed to provide funds to clean up the Great Lakes, once considered a good place to dump wastes with insufficient prior knowledge of levels, mechanisms, and fates.

Composition of Municipal Wastes

In studying the problem of safe and practical disposal of municipal wastes, it would seem that a first question requiring reliable data acquisition would be what is the material to be disposed of? What is its chemical composition? This, however, was not the order of data acquisition. The use of secondary (biological) sewage treatment plants preceded the systematic analysis of wastes by a long time (Sawyer, 1965). The earliest reasonably complete attempt at a domestic sewage analysis found was that of Painter and Viney (1959)[(1)]*. This contribution from the Water Pollution Research Laboratory, Stevenage (Herts), describes the organic composition of whole domestic sewage from a new town. Four physically separated fractions, settling, centrifugating, candle filtration, and filtrate were analysed. Presumably, the three solids fractions would parallel the solids utilized in the pioneer effort

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*Superscript numbers accompanying references, e.g., Painter and Viney (1959)[(1)], refer to a table or figure excerpted from the reference and collected in the Appendix, q.v.

in the USA by Heukelekian and co-workers (Hunter, 1965[2]; Heukelekian, 1959[3]).

Almost all the work done on characterizing and estimating the components of municipal sewage effluents has been carried out with some other end in mind than a simple, detailed specification of that composition.

Painter (1958)[4] had previously examined the same new town municipal sewage for inorganic composition. In spite of the detailed effort and careful examination by Painter and of Heukelekian, et al., it is clear they only account for at most 65-80 percent of the gross organics (on this point, see also Bunch, 1964); they made no attempt to describe the trace organic compounds (TC), and they were severely conditioned by the overall engineering requirements for materials handling on the large scale. Furthermore, they had a need to know the gross chemical composition of their substrate in terms of C, N, P, since that, so far as contemporary sanitary engineering thinking was concerned, was the problem. A review of eutrophication history (Stewart, 1967) shows this thinking to be typical also of the other disciplines involved. Although it was at about this time that oceanographers and marine microbiologists became aware of the probable role of TM, this was still new and not yet generally disseminated. Painter and Viney (1959) and Heukelekian (1959) seem unaware of these implications, but Vallentyne (1957)[5], writing

on organic composition of a variety of substrates, seems aware of the possible importance of sewage TM in ecological questions.

Painter (1958)[4] analyzed, for inorganic composition, the Stevenage new town sewage based on evaporation to dryness, and without fractionation of the total dried solids determined the major ions. This procedure not only abandons the possible development of information on speciation which is essential to understanding the role of TE, but only gives an approximate view of the gross inorganic composition, as well. As will be shown, later, more detailed inorganic analysis in the USA, while apparently containing much more information, in reality does not offer much beyond Painter (1958).

"Organic" Analyses of Sewage Effluents

J. R. Vallentyne (1957), in a review directed toward the biochemical aspects of ecology, listed known molecular forms of organic matter found in lakes and oceans and in terrestrial soils and sewage. He discussed the probable nature of organic substances known to exist, but whose composition or compositions had not yet been established - toxins and materials secreted or excreted by phytoplankton which apparently determined succession of other plankton or even in the case of *Gymnodinium breve* (red tide organisms), the viability of higher forms in the area (Dragovich, 1961).

It is impractical to review a literature review for detailed information contained. The reader, concerned with essential background for any experimental approach to the fate and possible effects of sewage on neritic waters and sediments and on the biota in the neritic zone, should certainly have available for reference Vallentyne (1957), Raymont (1966), and Provasoli (1963).

One conclusion we have drawn from Vallentyne (1957), Raymont (1966), and Provasoli (1963), inter alia, is simply this: whenever the question arises: does a given class of TC occur in sewage, detailed examination will probably show it, or its precursors to exist in various waste waters. A specific TC material may not have been experimentally demonstrated in waste, but it is not safe to conclude that it is not present. The question is, how much is present and what possible mechanisms are available for its fate. The balance of TE and TC in a given coastal situation and the needs of the desirable versus undesirable biota constitute the relations to be determined by chemistry and biology. Vallentyne (1956) has a succinct statement *in re* Pütters Hypothesis*. "The hypothesis has never been rigorously tested even though excellent tools are now available (isotopes, microfilters, chromatography)." This is now (1969) no longer a controversial matter. The question now is the delineation of the detailed mechanisms and quantities.

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*Putters Hypothesis is that lower forms ingest a significant amount of their food (energy) via dissolved organics.

Heukelekian and Balmat (1959) and Hunter and Heukelekian (1965) represent two reasonable analyses of the organic composition of sewage. In the first (Heukelekian and Balmat, 1959) it was recognized that protein, carbohydrate, and fat occur in sewage, but that detailed compositional data were unavailable. They examined the gross organic constituents occurring as solids, namely settleable, supracolloidal, and colloidal.

Hunter and Heukelekian (1965) pointed out that prior examinations of wastewater organic composition generally concerned the detection and composition of individual compounds of a particular interest. This is a limited approach and, of course, leaves most of the individual wastewater organic compounds (especially TC) undetected. Using a typical residential community sewage, they performed careful composite sampling and analyzed all fractions. While their results are still in the sanitary engineering vein, lumping together types of material (grease - 7%; amino acids - 19%; carbohydrates - 24%, in particulate fraction), because the engineering problem of large scale materials handling as a physical process is the important question for this work, the results are reasonably detailed and show that the composition, *mutatis mutandis*, is very like the composition of the British sludge samples (Painter, 1959).

Minor constituents (TC) mentioned, sterols, vitamins, creatine-creatinine, etc., are not examined quantitatively.

Murtaugh and Bunch (1965)[6] analyzed for the acidic components of sewage effluent and river waters; the acidic components from a variety of secondary plant effluents were described. Some of the fatty acids observed are known to coordinate some of the TE of interest; some of the lower fatty acids constitute stages in the metabolism of high molecular weight materials down to ultimate CO_2. How they will figure in the metabolic pathways in a given coastal situation is still to be determined (Provasoli, 1963). What the effect is, of compounds of this nature on TE en route to the coast is unknown.

A somewhat more detailed examination of the organic components of sludge was made by Teletzke, et al. (1966)[7] who examined the products of low temperature oxidation of sludge in order to determine the nature of the solids residue (the liquid being "accessible" to biological processing and, therefore, of no interest to them) in order to devise satisfactory procedures for further treatment. Assuming, with the APHA Standard Methods (1965), that proteins sugars, starch, lipids, and crude fibers were the principal constituents (by mass), that was what was determined in their analyses. Nucleic acids, with their considerable potential for biological activity, were ignored as relatively unimportant. An observation made, was that among the reactions occurring was hydrolysis of proteins to free amino acids (FAA) an observation of significance in any planned coastal disposal of the products of waste treatment processes (Clark, 1969)[8]. Unfortunately, the work of Teletzke (1966) is upon a

sludge that has been subjected to heat and oxygen, and while suggestive, has only an oblique relevance here.

Inorganic and TE Analyses

Numerous reports of analyses for a selected group of TE occur in the U.S.A. and other literature, but all are subject to serious question, so that this subject must be considered an open matter. For example, one of the most completely documented, apparently, sets of TE analysis data is that of the Hyperion outfall system in Santa Monica Bay, California, as described by Hume, Gunnerson, and Imel (1962)[9] and later Bargman and Parkhurst (unpublished compilation, 1969)[10]. In the Hume-Gunnerson (1962) data, the Hyperion TE composition is described in detail in time sequences: up to September 1957, present data 1957-1960, and projected data 1960 et.seq. All the tables bear an astonishing reproducibility of the TE data (the 1957 table is appended) "observed" for a series of TE estimates in a large tributary population in an industrialized metropolitan area. At the time these data were taken, no attempt at speciation was made in the absence of prevailing suspicions that this might be of mechanistic importance.

TE Analyses

In the U.S.A., R. N. Thompson, et al. (1964)[11] examined the effluent analysis data from a large number of sewage treatment plants using at least some form of secondary treatment. They

concluded, "Numerous studies of the gross composition of sludge have been made, usually with the soil building capabilities in mind." They mention some comparisons of C, N, P, and of ash content of various sludges, but conclude that "although isolated reports have been made on the exact inorganic chemical composition of sludge, comprehensive studies are apparently lacking."

They undertook a detailed spectrographic analysis* of air-dried sewage sludge with no provision for distinguishing inorganically from organically bound metal atoms. However, this work constitutes a real advance over the previous dearth of reliable data. While some of the internal ratios of elements are apparently inconsistent, it is believed their results represent a fairly good and complete list of TE in the "organic" composition of sludges.

Other TE analyses have been carried out by various workers interested in the ground water recharge, agricultural use of sewage (Wilson, 1968)[12], and the TE content of rivers as they approach the sea (Turekian, 1965, et seq.)[13]. These results are of general interest, but the data cannot be extrapolated to coastal waters since en route to the coast, the average TE composition and the relative TE composition and speciation will change, as will the particulate burden and its adsorbed TE. For example, the data of Turekian (1965, 1968), the data from Wilson (1968), and the Hyperion data are noticeably variant. Is this due to the differences in original sources, the

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*Certainly reliable to one order of magnitude.

differences in the particulate chemistry, or the differences in the dissolved organics, or possibly, the methods of analysis employed? Assuming reliable estimates on the part of each set of experiments, it may be possible to understand the mechanisms of interaction and change of TE composition of waters on their way to the sea.

Neale (1964)[14] presents the more common inorganic constituents of some 22 typical municipal water supplies and then through effluent analytical data for these cities' sewage plants shows the mineral increment per once through domestic usage. His interest, the sanitary engineering of distillation purification plants depending on such effluent supplies for input with concomitant scaling problems, restricts his examination of effluent composition to the major components and to such catch-all specifications as hardness, alkalinity, total solids.

Outright errors and internal inconsistencies (lack of material balance) are to be noted in these tables, but the tables are reproduced in the Appendix as among the best available data of this kind.

An interesting comparison would be the natural waters TE composition and the TE composition of sewage generated in the population dependent on those natural waters. To some extent, (Turekian, 1965-1968; Livingstone, 1963; Wilson, Becket, 1968; and Bunch, Ettinger, 1964) this has been carried out.

A comparison of Hyperion outfall TE and the seawater TE concentration isopleths in the vicinity is not available, but would be most illuminating for ecological comparisons.

Since the TE elementary composition of sewage is largely a reflection of TE composition of the original natural water supply in the locale, it might be supposed they are similar (but not congruent) in the geometric sense. This is a view implicitly assumed by various workers (Bunch, 1964; Wilson, 1968; Eckenfelder, 1969) who compiled data on trace element increments in once-through domestic usage. The organic complexity of sewage effluents as compared to most municipal water supplies (similarities may occur for natural water supplies - Vallentyne, 1957) means that the TE binding to particulates (Turekian, 1967) to chelate systems (Duursma, 1966) and speciation in general, must be reevaluated (NASCO-NAECO, 1969). Perhaps the same question should be raised concerning TC.

In general, the trace element composition of the wastewater is related to that of the natural waters in the vicinity and these have been tabulated (Livingstone, 1963; Turekian, 1965; and Bowen, 1966). As is to be expected, the relative concentrations will vary somewhat, since there are other inputs to human diet and since man, no less than mollusca, can concentrate some atoms. And, of course, the concentrations in wastewaters will be increased over the natural waters (Bunch, 1964). Changes in proportions are masked by the

presence of large quantities of water with its TE content, but we expect changes. Put in more familiar terms, this means that the concentration of specific TE by the metabolic processes of organisms is now a well-recognized phenomenon. (Nelson and Evans, 1969; Radioactive Wastes, 1966).

Another change to be expected is that the organic linkages of the TE must certainly change. The enzyme cofactor relations, co-ordinate complexes with amino acids, chelate compounds, the relation of TE to surfactants, all these speciation considerations must be significant to subsequent mechanisms in ecological consequences. However, no information was found.

However, the reverse case, the action of TE on the processes occurring in secondary plants has been investigated from the sanitary engineering point of view -- does a slug input of a particular ion interfere with the normal operation of a (activated sludge process) sewage treatment plant? This proposition was considered for a number of ions (Ettinger, 1965) without regard for mechanisms, and it was shown that ultimately the slug input was passed on and the plant resumed its previous efficiency. Long-term input was not carried out nor was speciation of input considered.

Apparently, no one has asked what the effect would be of large scale inputs of TM via sewage effluent systems to coastal waters, although some comparisons have been made of ocean sediment organic content and sewage organic content (Vallentyne, 1957).

As this report was in press, there appeared a news report on the establishment of classes of biodegradability for various synthetic organics passing through typical activated sludge plants (Buzzell, 1969). About 7 out of 22 classes were appreciably passed by the plant, though in batch processing they were more susceptible. No detailed information was available on trace materials.

TE Content of Seawater

The overall trace element analysis of seawater, while in far from complete form, especially in near coastal zones, is in a reasonably useful stage. The compilation of Bowen (1966)[15] is very useful, the analytical methods and compilation of Chow (1968)[16] more specifically addressed to oceanography and pollution, is a particularly valuable review. Goldberg's chapters (1961, 1963) also are useful summaries and discussions of the minor elements (TE in our notation). Turekian (1965)[13] has summarized the TE content of certain rivers and their TE input from industries as the rivers approach the coast.

Influence of Sea Borne TM

One estuary of some considerable size, and a freshwater flow of some magnitude, where sewage plant effluent is planned for the near future as a significant fraction of average flow, and possibly much greater than lower flow values, is the Duwamish estuary above Puget Sound (Gibbs, 1968; Welch, 1968). The Duwamish is fed by the

Green River from the Cascade Mountains at 340-20,000 m^3/min. The mean flow is reported (Welch, 1968) as 1,700 m^3/min.

Welch says that the proposed ultimate capacity of the plant is to be 545,000 m^3/d (about 380 m^3/min., but subject, obviously, to time of day minimum-maximum variations.

A simple study of the phytoplankton "blooms" in the estuary as effected by the addition of unspecified nutrients was carried out to determine whether these were more prevalent or of greater intensity after the installation of the Renton Treatment Plant.

The known high "nutrient" content of the receiving waters led Welch to suggest as a working hypothesis that "barring a radical change in species dominance, additional mineral nutrient from the Renton Plant might not alter the timing of phytoplankton blooms, but that the maximum biomass produced during a bloom could increase."

This reasonable hypothesis contains two admissions of our ignorance of the mechanisms involved:

"Barring a radical change in species dominance" translates into we do not at present know why or how changes in species dominance occur and cannot, therefore, predict the outcome of a very substantial increment of effluent. And, "might not alter the timing ...but maximum biomass...could increase" translates into we do not know the timing and rate controlling steps, nor the biomass culmination dependence and so we cannot predict the effect of the sewage effluent.

The study using phosphate/nitrate ratios and chlorophyl a observations at various stations over seasonal variations showed that the chlorophyl did not increase where the "nutrients" were greatest, but did increase markedly lower in the estuary where nutrients were supposedly lower in concentration. The suggestion was made that these phenomena represent the results of fresh water at the upper reaches versus salt water introduced at the lower reaches. The possible importance of trace materials was recognized, but with no discussion. However, some data on trace elements at the station of greatest phytoplankton abundance are given. No mention was made of the possible introduction of control, catalytic, or limiting nutrients with the salt water entering the lower estuary.

Physical factors (light intensity, water column stability, D.O.) were considered, but these did not clearly influence blooms from place to place in the Duwamish estuary. The discussion concentrated on "nutrients" and it was claimed that there was no difference in mean total phosphate concentration during the three summers of observations, but that the tidal prism was better correlated to timing of the bloom initiation and biomass achieved correlated best to the time over which the tidal prism remained high relative to the fresh water input. No mechanism is suggested, but the tidal importation of relevant materials cannot be ignored as a good possibility.

Young, et al. (1967) examined the question of the biodegradability of organics which increase continually in number, complexity, and potential for ecological effects. They measured the biodegradability of classes of organics by relative rates of TOC or COD disappearance versus oxygen uptake and total bacterial growth using a small wastewater inoculum and allowing sufficient time for "acclimation." "Acclimation" may have meant that a single species present grew in and did essentially all the biodegrading, the species varying from material to material, since, acclimation times varied.

No consideration was given to possible complexities arising in a natural locale where many other species and components (TE and TC) might be present.

II.

SOME MECHANISMS OF TM IN COASTAL WATERS

Evaluation of pollutants at low concentration and their chemical and biological interaction is difficult on two scores:

1. The problem of detection of the long term "subtle effects" is even more tedious and difficult in epidemiological theory and practice than determination of the more familiar LD_{50}, a severe problem in its own right (Waldichuk, 1968). Forensic methods involving histochemistry, blood serum electrophoresis, hematrocrit, and other hematological examinations, enzyme activity inhibition, are all available for such studies. All are of substantial complexity in the doing and in the interpretation. Examples are known of avoidance and the like, effects on learning capacity, aggressiveness, territorialism and courting. M. Blumer (1969) commented that many marine animals produce minute amounts of chemicals that perform functions essential to maintaining the cycle of life. These chemicals act as attractants during the mating process. They aid predators in locating their prey, and conversely, give warning to potential victims that they are being stalked by predators. Oil - whether from a single big spill or a buildup of repeated small doses - may well upset these vital chemically-triggered processes.

The above paragraph mentions the effects possible on forms higher in the phyla. But the ecological relationship of lower

forms ingesting (and excreting) minute amounts of key TC and TE from colleague and precedent forms may have their normal metabolic behavior made impossible with potentially catastrophic results.

Recognizing the fact of our ignorance of the details of these processes (Provasoli, 1963) emphasizes the dangers of proceeding. Surely ignorance here, where we are introducing a large variety of TC and TE from every outfall and barge dump operation, is no basis for optimism.

2. The chemistry of detecting, characterizing, and quantitating micro amounts of relevant TC is one of considerable difficulty (Park, 1962; Jeffreys and Hood, 1958; and Clark, 1969), while the estimation of TE is of such complexity and experimental difficulty that only intercomparison of results by a variety of methods can lead to a degree of confidence (Bowen, 1966).

The effects of substantial additions of specific pollutants on various biota has, of course, a large literature (Sharp, 1969). These evaluations of higher animal susceptibilities to gross pollution or to specific poisonous materials constitutes an important area not dealt with in this work. In addition, no discussion is given here concerning the profound chemical and biological reaction changes which may be induced by changes in the thermodynamic variables, such as temperature, radiation, ionic strength (Cawley, 1969). Similarly, the effects of gross organic pollution via sewage input, reduction in D.O., sewage sediment

deposits with anaerobic phenomena (H_2S production, concentration of iron), have all been noted near sewer outfalls or at barge sludge dumping operations. Only Vallentyne (1957) has attempted a comparison of the organic TC of coastal and fresh waters with the possible input from sewage. The impact for microorganics (TC) as for TE would be:

(a) Strangeness (no previous experience of the species with the material)

(b) Concentration possibilities

(c) Metabolic interferences (stimulatory or inhibitory)

One very practical reason that more is not known about TC and their effects in the coastal zone is that, not only do these change from place to place, but also at each point a complete description might be a life's work addressed to subtle effects and complicated chemical questions. Yet, the instance of DDT present in very low concentrations indicates such information is essential. The world wide subtle effects* from TC in sewage may, as in the case of DDT, affect the world ocean even where the local dramatic effect*

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*We distinguish here two phenomena: In one, the local dramatic effect, a violent noxious material may kill 1 or 1000 individuals in a strictly local catastrophic event. Natural degradation prevents widespread disaster. In the other, the world wide subtle effect leads to no immediately newsworthy results and remains open to discussion for long periods. The physical and chemical differences which lead to these distinct possibilities are, among others, low biodegradability, accumulation from low concentrations in the environment by biota, passage and concentration up the food chain, key metabolic effects as hormone or enzyme reactions interferences, all of these apparently were the case for DDT and related compounds.

does not occur. The analogy to the DDT case for trace compounds put into the marine environment is a distinct possibility.

Goldberg (to be published) quotes the well-known saying, "For every chemical element, there is at least one planktonic species capable of spectacularly concentrating it." Then extrapolating to other chemical material inputs to the oceans, he suggests some species will occur for taking up each modern technologically advanced material. This is undoubtedly an open question. Based on given clones in existence and the synthesis of new exotic materials, never before in existence, the chance of many of these establishing a beneficial rapport seems small indeed. Certainly, the situation is not analogous to the TE case where the TE have always co-existed with the evolving clones which have genetically determined abilities to accept, reject, or concentrate TE.

In my opinion, the specificity of most biochemical reactions rules out any general tolerance situation but massive introduction of strange materials to a given area will probably always result in changes in the clones, numbers and types. In the case of low level or TM introduction, it is to be expected that these same principles apply but due to our present lack of experience, we cannot predict steady-state concentrations of either material or respondent.

On the other hand, it is just this specificity which allows us to state there is a theoretical possibility of the use of "guidance and control materials" in an area rather than biocidal material or

surplus undesired nutrient. What these will be for any given habitat remains to be demonstrated.

The fallacies in considering the oceans as infinite sinks, therefore, are:

1. We do not have detailed knowledge of input, inventory, removal for most trace materials (TM)(Bowen, 1966; Goldberg, 1965).
2. We do not have detailed knowledge of their interactions with the biota (Provasoli, 1963; Raymont, 1966).
3. We tacitly assume the TM put into neritic and estuarial waters will be mixed quickly, removed permanently to the sediment or the deep ocean. Both of these removal mechanisms are probably not beneficially operative in determining the fate of the TM introduced (Turekian, 1965; Postma, 1967).

In actual fact, recycling by benthic biota of TM from sediments may be a most important mechanism tending toward long term availability of TE from the inventory in the sediment (Hood, 1969). In addition, it is now suspected that the deep ocean is actually supplying TM to the coastal zone (Turekian, 1965) rather than acting as a sink. Postma (1967) has described physical processes occurring in estuaries that could account for these observations.

We have noted (Provasoli, 1963) that we are dealing with inorganic TE requirements and resentments and with organic TC requirements and resentments. Stimulation, inhibition, poisoning, and feeding regulation have all been described for individual cases. We have noted (Waldichuk, 1969) that the methodology of evaluation of long-term low-level pollution is not neat and quantitative, but needs considerable work.

The specificity of species enhancement noted in most cases of pollution has been undesirable species at the expense of desired species; but there seems no reason in theory why by proper and judicious management, the beneficial species could not be enhanced at the expense of the undesirable species.

III.

SOME ASPECTS OF TM IN ESTUARINE AND COASTAL WATERS

The question of trace materials in the marine environment is no longer - do any species use dilute dissolved material as energy sources, but which species prefer which compounds and to what extent can they obtain the required energy in this way, and what are the rate controlling steps? Such usage seems confirmed as high up the phylla as Enchinodermata, in which instance work is presently underway (M. Clark, 1969). One may speculate on the results of a knowledge of the dissolved organics preferences of the steps culminating in a predatory fish. The food web is pyramidal[18] in the folklore of salmon and trout nutrition. In a web, alternate pathways of equivalent efficiency occur and interferences at one point cannot stop ultimate propagation of the end product species. But in fact, it is most selective at each level constituting more of a chain[19] or a network of preferred time sequential interlocking reticules* (with possibly a greater number entering at the base). In a chain, there are a number of points at which interference can have substantial effect on ultimate propagation of the end product species. If we assume ecological interdependencies other than the food pyramid -

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*One is tempted to use the Johnsonian definition of a net.

metabolic contributors of other kinds - odors, sizes of food particles, poisons, antibiotics, the chance of control and of the useful use of wastewater increases substantially. For the trout or salmon, often successful in apparently oligotrophic surroundings, it is apparent that addition of gross nutrients is not the whole story (Powers, 1969) (See page 39, Mansueti *in re* Sea Bass).

Cronin (1967) presents some ideas on specificity, balance, and control by means of nutrient, catalytic, and TM control. These ideas may also apply to use of selected biocide materials (Butler, 1963) since competitive species may be differentially affected by small quantities of one or other biocide. The design of "competition biocides" systems may be as simple as addition of a vitamin required by one of the species to elaborate toxin or hormonal additions to prevent regeneration in one, but not the other species.

Cronin (1967) points out the significant variation between species' response to classes of chemical materials and says that irregularity in the results of field tests suggests the reasonable probability that actual toxicity might be affected by temperature, silt, flushing rates, salinity, and other environmental factors. Under the designation "other" one might well suspect ecologically determined nutrition and metabolic responses. So, species A, A' ..., not affected much in laboratory experiments while B, B'..., are affected. In the field, however, the effects on species C, C' ..., must have some feedback effect on the relative reactions of A and B.

The competitive synthesis (in a single exponentially growing species) of protein and carbohydrate is a severely conditioned matter depending on availability of various nutritional materials even while the apparent C^{14} rate is a constant. Thus, the availability of metabolites, natural or waste product, may be affecting the overall productivity in ways that have not been measured by C^{14} procedures and over long periods not previously considered.

During photosynthesis, it is well known (Fogg, 1964; Burke, 1962) that synthetic material is liberated in the water. The significance attributed to these materials in determining bloom succession patterns may indicate how direction and control may be achieved by application of the information we ought to have before placing large amounts of wastes in ocean locations.

Wood (1967) in discussing the cycling of nutritional elements from sediments to supernate waters points out that bacteria are obviously not doing it all: he dismisses the colorless protozoa as unimportant in this overall processes. See, however, Johannes (1965), a reference Wood seems aware of, but not in this context.

The benthic recycling of chemical species plays a role in the diagenesis of estuarial sediments and vice versa (Hood, 1969). The elucidation of these chemical reaction possibilities remains an essential problem.

The regeneration of nutrients by biochemical action in sediments is, of course, only the positive aspect of the problem. Gahler (1969) observed that sediment from Klamath Lake could be used in laboratory plankton (*Selenastrum*) growth studies (stirring the sediment presumably allowed escape of the nutrients to the supernate water, but there are other possibilities); but sediments from Woahinke Lake diminished the growth of *Selenastrum* in lake water, which without the presence of the sediment did support growth*. The more detailed experiments, at various ocean locations, of Johnston (1963, 1964) offer some clues as to what processes may be occurring.

What the results would have been for species other than *Selenastrum* cannot be specified, but Lackey, at a seminar, quoted in Symons (1964) was aware that the question of nutrients versus species specificity could lead to complex relations. "When we note the condition of blooms in the field, it is at once apparent that there is much variation of the conditions under which they appear, and at best our knowledge of what nutrient substance and amounts are related to algal densities is merely a guess.

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*One possible explanation offered by these workers is "manganese" known to be present in Woahinke sediments; however, manganese is a prerequisite for photosynthesis. The conclusion here would seem to turn on concentration, speciation, and availability of some trace material.

"There has been considerable discussion of the possibility of removing $PO_4^{\equiv}$ from the effluents of conventional treatment plants. It is suggested here that this may change only the composition of the bloom. There are algae whose $PO_4^{\equiv}$ requirements are extremely low, below the concentration which might remain after treatment." Lackey evidently conceived of the source of "P" as only inorganically bound "P" coming from effluent. Organically bound "P", directly used, or subject to ultimate mineralization or emanating from sediment, was not part of his scheme, but its existence reinforces his thesis.

Provasoli (1963) points out that a number of species do very well on organic "P" compounds (no apparent inorganic "P" requirement) and this may in part account for rapid bloom succession based on quickly available "P", rather than waiting for complete degradation to mineral "P". Not many studies have been made of this speciation phenomenon which is of considerable mechanistic interest. The standard method for "P" as ortho-phosphate will not detect organically bound "P", in general (Standard Methods, 1965).

The secondary treatment of wastes familiarly referred to as "the mineralization" (reduction of BOD) quite possibly results in the organic-metal atom fixing of TE in the same general way as P and N are reduced from soluble inorganics and organics to insoluble sludge-borne compounds (unfortunately not a 100 percent processes).

Hanes and White (1968) showed that seawater concentration affects the oxygen uptake rate of a benthal system in an estuary. They also showed that addition of "nutrients" from sewage treatment plant sludge increased the oxygen uptake by the benthic system regardless of the salinity of the supernate water, but the effect was greater for greater concentration of seawater implying the seawater contributed some key material as was inferred from the sludge only addition.

Carriker (1967) has discussed the estuary ecology with particular emphasis on the oceanic input to the estuary. The significance of chelation of TE on plankton at various oceanic locations has been discussed at length (Johnston, 1963, 1964). But Duursma (1966) claims chelation is relatively unimportant though he claims "some effect" and suggests free amino acids, for example, may be effective. Free amino acids are an identified set of TC in all sewage and their possible effects on specific ecological systems may be most significant (Clark, 1969), either as key nutrients, control media as chelators, or other pathway contributors.

Growth factors and organic control and/or specific metabolic accelerations are exemplified by the chelating material that makes iron "available." Presumably, this occurs by simply increasing the total dissolved iron as against previously insoluble iron, though a pathway of lower activation energy requirement, or provision of a sterically advantageous route are also possible. Either of the two

mechanisms for getting iron across the cell wall would jibe with geometric specificity of biochemical reactions. At any rate, such a material is a metabolic "control" rather than a nutrient. It is also apt to be a concentration, pH, and ionic strength dependent rate controlling step. If it is a control mechanism and itself a controllable step, the way to use it for overall guidance and control seems apparent. Therefore, we say: to speak loosely of the gross P, N, C input to coastal waters cannot be the whole story for these elements appear in various molecular arrangements rather than as the elements. Thus, carbohydrates, protein, fats (and lipids in general) must be covered in any working hypothesis of mechanisms of appearance and disappearance of species. Furthermore, without a concurrent explanation of TM, vitamins and other substances, no coherent story is possible.

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IV.

THE SAWDUST MULCH PROBLEM AND THE POSSIBLE USE OF WASTES: GUIDANCE AND CONTROL

The "sawdust mulch problem" is a familiar one to the home gardener, whereas the professional and the academic may have once recognized it, but are now off on other tangents and have left this important problem to the organic gardener and other *doctrinaires*.

Briefly stated, the sawdust mulch problem arises from the use of organic mulch to improve the tilth of soils for agricultural use. The plowing under of green manures being perhaps better but slower, the addition of manure is experimentally practical and desirable; the growth of the microorganisms which mediate the agricultural chemistry of the soil is enhanced, water absorption is increased, plant roots have better bedding, and in general, numerous desirable ends are served by adding such mulches to the surface or plowing them under. But the simple observed fact is that sawdust actually holds up the growth of plants. As is well known, the sufficient answer to this problem is that the organisms using the sawdust (breaking it down) also use up the immediately available nitrogen compounds. Given sufficient time, cycling of all of the nutrients would make it available again, but the immediate need is for the addition of nitrogen fertilizer. If we are going to reinforce the organic manures -

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secondary plant sludges for example - we can get the same or even faster response from the added fertilizer alone. Or, on a dollar basis and for the short term, it is better to omit the organic manure and use the familiar N, P, K, inorganic fertilizer which generally contains TE or to which TE can be readily added. It can be argued that the situation, based on history (Euphrates Valley) and on projection (Lake Mead irrigation) is more complex than that simple solution contemplates. Be that as it may, a conclusion for the useful addition of wastewaters to agricultural lands (Wilson, 1968) or to coastal and estuarine waters is this: to obtain a desired result, the propagation of desired forms* - we may need to revise the TE or TC balance or availability via chemical manipulation in the same way we have to provide nitrogen in the sawdust mulch instance.

Control of the available inorganic nitrogen and phosphorus may be useful, but not sufficient, mechanistically speaking, in coastal waters where the available data suggest that N, rather

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*Fertilization which enhances the biomass by substituting thistleweed for corn is not a desirable state of fertility. Initiation and sustenance of a bloom comprised of *Gymnodinium breve* is an obvious bad result. There are certainly more subtle, longer term, TM relations to be considered. Change in species present in coastal waters is exemplified by the replacement of *Nitzschia* by *Nannochloris atomus* and by *Stichococcus sp.* shown (Ryther, 1954) to occur in Moriches Bay. These, in turn, are known to be undesirable as food (Ketchum, 1967). In short, they are weeds growing rapidly where the balance of added fertilizer is somehow wrong.

than P, is the limiting macronutrient and where organic compounds of these materials offer alternate pathways. Additionally, the interaction of these macronutrients with TE may be the rate controlling steps in complex overall situations. For example, *Gymnodinium breve* concentrates titanium and zirconium, two somewhat unusual TE so far as living forms are concerned. But these two are among the ones best co-precipitated with $PO_4^{\equiv}$ introduced as the salt of or into iron and calcium containing waters. Why this species blooms off the Florida coast and its relation to the phosphate content of runoff waters from Florida would suggest an interesting relation involving TE mechanisms (Dragovich, 1961). It has been suggested (Morgan, 1969) that the red tide is a natural phenomenon and as such, one that water pollution workers will not wish to spend their efforts in studying. It might be asked what is natural, and what is unnatural? If the red tide mechanism is fully understood as a result of research, wouldn't this help us to understand the mechanisms of waste induced or supported blooms and enable us to avoid undesirable blooms? In the introduction, we have emphasized that the chemical and biological processes we need to understand are all "natural" processes.

We need to know the details of the individual food web, chains, cycles, and alternative pathways in considerably greater detail than we do at present.

The basic Monod relationships and mechanisms of limiting nutrient depend on a variety of mechanisms*. Thus, inorganic phosphate may be limiting or not, depending on availability of organic phosphorus. Further, in recycling via the earthworm effect** the organics may be available much sooner than the ultimately mineralized phosphorus. Mediating forms (chelates for TE) will depend on pH rather sensitively. The cycling of materials via the earthworm effect will be dependent on what else is available. To make the proper TM, whether micro iron or vitamin B_{12} or biotin, available to desired phytoplankton, may require that we add additional or other TM to the milieu.

Consider the graphs depicting the very specific eating habits of some desirable pelagic biota (Green, 1968)[20]. If we wish phytoplankton M_i to be available to feed (i.e., be part of the chain leading to) *Micropogon undulatus* (Atlantic croaker) or *Anchoa mitchilli* (bay anchovy) to provide for the predatory fish we wish to propagate, then we must provide TM (M_i) to that benthic organism which recycles the TM (M_i) required by the phytoplankton M_i. The

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*Like the Steeman-Nielsen C^{14} measurements of "productivity" these observations of a resultant must be interpreted in terms of internal mechanisms; in our view often the outcome of TM mechanisms.

**The "earthworm effect" is the overall benthic recycling of nutrient elements from within the sediment to the surface of the sediment and vice versa. This mechanism is, of course, part and parcel of the chemical mechanisms prevailing there.

addition of wastes containing nutrients favoring still other webs or chains from the benthos onward based on TM (M_j) will not help propagate the predator fish feeding on *Micropogon undulatus* or on *Anchoa mitchilli*, but by a variety of mechanisms will hinder their propagation.

Wood (1967) asks what phytoplankton and zooplankton are preferred by what fish. To some extent, ecologists are recognizing the importance of this question (Green, 1968) and it is clear that the older idea of food webs is not sufficient. The idea of food chains must be utilized also in attempting to predict the pelagic outcome of benthic waste sediment chemical reactions.

Mansueti (1961) described the apparent increase in a desirable fish population in an important estuary with a number of tributaries. No mechanisms related to nutrients or other relevant materials were offered other than a correlation of estimates of fish taken in a number of years and of population growth in the watershed supplying the terrigenous waters. Whether, in fact, a fish production growth curve was observed in the period of population growth is moot; the important thing is that such an outcome is desirable and possible.

McHugh (1967) has discussed the estuarine nekton from the point of view of food cycles, energy exchange, and biological productivity (i.e., desirable useful productivity). The feeding of soluble organics, labeled as required, at various levels of nutrition (energy content) could be used in experiments parallel-

to the familiar C^{14} primary productivity measurement, but more incisive. The C^{14} method is an overall measurement - a resultant of competing or additive reactions and details of mechanisms prevailing and controlling specificity and dominance are not directly obtained. By the use of sets of organics chosen for the milieu and the competitive plankton under study, some further insight would be obtained. The methodology of such experiments is well worked out (Young, 1967). We should note in this regard that Wood (1967) points out that the relative rates of photosynthesis and dissolved organic uptake is in favor of the uptake when light available is low. Then such possible heterotrophic mechanisms for use of abundant natural and waste organics in estuaries become significant questions.

V.

APPENDIX

1. Painter, 1959

COMPOSITION OF WHOLE SEWAGE

Constituent	Concentration in Whole Sewage (p.p.m. carbon)					
	Sample 2			Sample 3		
	In Solution	In Suspension	TOTAL	In Solution	In Suspension	TOTAL
Carbohydrates - total	21	12	33	40	15	55
Amino acids - free	2	0	2	5	0	5
- bound	6	19.5	25.5	8	23	31
Higher fatty acids	0	74	74	0	71	71
Soluble acids	28.5	6.0	34.5	17	4	21
Esters	0	37.2	37.2	0	28.2	28.2
Anionic surface-active agents	12	5	17	11	3	14
Amino sugars	0	0.9	0.9	0	0.5	0.5
Amide	0	1.2	1.2	0	1.5	1.5
Creatinine	2.7	0	2.7	3.5	0	3.5
Total - by analysis	82	218	300	106	205	311
- by addition	72.2	155.8	228	84.5	146.2	230.7
Proportion accounted for, %	88.0	71.4	76.0	79.7	71.3	74.2

1. Painter, 1959

COMPOSITION OF SUSPENDED SOLIDS FROM SEWAGE
(Figures in brackets are the ratios of hexose to pentose)

	Concentration, Expressed as Carbon of Total Carbon, %					
	Settled Solids, A		Centrifuged Solids, B		Candle-filtered Solids, C	
Constituent	Mean of 3 Determinations	RANGE	Mean of 3 Determinations	RANGE	Sample 2	Sample 3
Carbohydrates successively extracted by						
EtOH	1.9 (5.4)	1.5- 2.7	0.4 (1.4)	0 - 0.7	1.5 (1.5)	0.5 (1.4)
$HClO_4$	3.4 (2.2)	1.7- 4.5	1.4 (1.5)	0.6- 2.2	2.1 (1.4)	2.8 (1.5)
HCl	2.9 (2.0)	2.4- 3.3	1.6 (3.3)	1.2- 2.5	2.1 (3.5)	1.0 (5.0)
H_2SO_4	0.7 (2.5)	0.2- 1.6	0.3 (3.8)	0.1- 0.8	0.2 (3.0)	0.6 (5.0)
TOTAL	8.9 (2.6)	6.8-10.9	3.7 (2.1)	2.5- 4.8	5.9 (2.0)	4.0 (2.1)
Amino Acids - Combined	9.5	7.3-11.5	9.9	8.2-11.8	17.1	13.0
Acids - insoluble	25.5	11.5-35	31.9	25.0-38.6	33.8	35.8
- soluble	2.0	1.4- 2.4	3.2	2.5- 4.0	1.7	1.9
Esters	15.8	11.5-20.8	13.4	12.2-14.0	9.6	10.6
Anionic surface-active agents	1.3	0.5- 2.3	1.4	0.8- 1.8	3.2	1.8
Amino sugars	0.3	0.3- 0.3	0.2	0.1- 0.4	1.2	0.4
Total accounted for	63.3	45 -74.6	63.7	57.2-71.3	72.2	68.4

INDIVIDUAL SUGARS PRESENT IN FILTERED SEWAGE AND HYDROLYSED SUSPENDED SOLIDS

Sugar	Hydrolysed Settled Solids (A)	Hydrolysed Centrifuged Solids (B)	Hydrolysed Candle-Filtered Solids (C)	Candle Filtrate	
				Sample 1	Sample 2
Glucose	+++	+++	+++	51	16
Galactose	++	+	+	9	<3
Mannose	Trace	Trace	-	-	-
Lactose	-	-	-	13	17
Sucrose	-	-	-	16	63
Maltose	Trace	-	-	-	-
Arabinose	++	+	Trace	+	+
Xylose	+	+	+	+	+
Ribose	-	Trace	+	-	-
Rhamnose	+	+	++	-	-
Fucose	-	-	Trace	-	-
Fructose	-	-	-	++	+
Total Anthrone reacting	-	-		89	96

Note: The symbols give only a very rough indication of the proportion present. Numerical values under "candle filtrate" are percentages of anthrone-reacting sugars pipetted on to paper chromatogram.

2. Hunter, 1965

ANALYTICAL METHODS FOR DETERMINATION OF ORGANIC COMPONENTS OF WASTEWATER

Component	Source of Method	Remarks
Particulate fraction:		
Separation into groups	Balmat	
Total grease:		
Total acid-free grease	Scott	
Phospholipids	Bloor	
Total unsaponifiable matter	Association of Official Agricultural Chemists	
Constituents of unsaponifiable matter	Rosen and Middleton	
Cholesterol	Brown et al.	
Total glyceride fatty acids	Association of Official Agribultural Chemists	
Total free fatty acids	Scott	
Polyunsaturated fatty acids	Hausen and Wiese	Includes linoleic, linolenic, and arachidonic acids
Monosaturated fatty acids	Mueller	Oleic acid
Saturated fatty acids	Calculation	
Individual saturated fatty acids	Mueller	
Phenols	Faust and Aly	
Detergents	Kramer and Kroner	ABS

2. Hunter, 1965 (Cont.)

ANALYTICAL METHODS FOR DETERMINATION OF ORGANIC COMPONENTS OF WASTEWATER

Component	Source of Method	Remarks
Miscellaneous alcohol-soluble matter:		
Hexose	Neish	
Tannins	Standard Methods	
Nitrogenous matter	McKensie and Wallace	
Amino acids	Rosen	Alcohol-soluble matter prepared for analysis by 24-hour reflux with 6-N HCl, evaporation, and removal of NH_3.
Carbohydrates and lignin		
Pectin	Breston	
Hemicellulose	Breston	
Cellulose	Norman and Jenkins	
Lignin	Norman and Jenkins	
Alcohol-insoluble nitrogenous matter	Same as for alcohol-soluble nitrogenous matter	
Soluble Fraction		
Ethyl-ether-soluble group	Braus et al.	Separated into acids, bases, neutrals, and amphoterics; acids corrected for detergents, neutrals corrected for cholesterol

2. Hunter, 1965

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Monosaturated fatty acids	Mueller	Oleic acid
Saturated fatty acids	Calculation	
Individual saturated fatty acids	Mueller	
Phenols	Faust and Aly	
Detergents	Kramer and Kroner	ABS

2. Hunter, 1965 (Cont.)

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Lignin	Norman and Jenkins	
Alcohol-insoluble nitrogenous matter	Same as for alcohol-soluble nitrogenous matter	
Soluble Fraction		
Ethyl-ether-soluble group	Braus et al.	Separated into acids, bases, neutrals, and amphoterics; acids corrected for detergents, neutrals corrected for cholesterol

2. Hunter, 1965 (Cont.)

ANALYTICAL METHODS FOR DETERMINATION OF ORGANIC COMPONENTS OF WASTEWATER

Component	Source of Method	Remarks
Ethyl-ether-soluble group (cont.)		
Individual acids	Mueller et al	
Detergents	Kramer and Kroner	
Phenols	Faust and Aly	
Cholesterol	Brown et al.	
Indole and skatole	Rudolfs and Ingols	
Volatile acids	Heukelekian and Kaplovsky	
Individual volatile acids	Manganelli and Brofazi	
Ether-insoluble compounds:		
Hexose	Neish	
Pentose	Mejbaum as modified by Albaum and Umbreit	
Total amino acids	Rosen	After acid hydrolysis by method of Cummins and Harris
Creatine-creatinine	Bonses and Toussky	
Uric acid	Hawk, Oser, and Summerson	

2. Hunter, 1965

ORGANIC CONSTITUENTS OF THE ALCOHOL-SOLUBLE, ETHER-INSOLUBLE MATTER AS PERCENT OF FRACTION TOTAL SOLIDS

Organic Constituent	Winter-Spring, 1959			Fall-Winter, 1959-60		
	Settleable Fraction	Supracolloidal Fraction	Colloidal Fraction	Settleable Fraction	Supracolloidal Fraction	Colloidal Fraction
Amino acids	18.5	12.0	32.0	15.1	6.1	41.5
Sugars	4.6	5.5	4.9	4.1	7.0	8.0
Tannins	8.6	3.6	8.4	8.0	3.2	11.8
Undected*	68.3	78.9	54.7	72.8	83.7	38.7

*Corrected for ash content

2. Hunter, 1965

CONTRIBUTION OF THE NON-NITROGENEOUS, ALCOHOL-INSOLUBLE MATTER (CARBOHYDRATES AND LIGNIN) TO WHOLE SEWAGE

Organic Constituent	Winter-Spring, 1959			Fall-Winter, 1959-60		
	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)
Pectin	1.48	2.16	1.35	1.30	1.32	1.35
Hemicellulose	3.53	4.32	1.33	3.21	5.36	0.94
Cellulose	11.50	3.15	2.43	21.58	2.05	2.34
Lignin	1.54	0.97	0.98	1.66	0.58	1.20
Sum	18.05	10.60	6.09	27.75	9.31	5.83

2. Hunter, 1965

CONTRIBUTION OF THE PARTICULATE FRACTIONS TO WHOLE SEWAGE

Component	Winter-Spring, 1959			Fall-Winter, 1959-60		
	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)
Total grease	11.70	9.57	5.55	11.25	8.65	6.06
Alcohol-soluble matter*	4.62	2.01	1.40	4.93	1.83	0.70
Amino acids						
Alcohol-soluble	1.05	0.28	0.66	0.87	0.12	0.49
Alcohol-insoluble	7.54	12.56	4.71	11.54	12.14	4.27
Carbohydrates and lignin	18.05	10.60	6.09	27.75	9.31	5.83
Total organic matter	43.01	35.02	18.41	56.34	32.05	17.35
Volatile solids	52.25	41.29	20.64	63.89	36.86	18.79

*Not including amino acids

2. Hunter, 1959

ORGANIC CONSTITUENTS OF SOLUBLE FRACTIONS

Constituent	Winter-Spring, 1959		Fall-Winter, 1959-60	
	mg/l*	Percent†	mg/l*	Percent†
Ether-soluble — I				
Acids‡	22.56	9.25	33.95	11.91
Bases	3.24	1.33	3.55	1.25
Amphoterics	4.80	1.97	7.17	2.51
Neutrals§	13.59	5.57	17.31	6.07
Ether-soluble — II				
Detergents (ABS)	3.94	1.62	4.02	1.41
Phenols	0.12	0.05	0.10	0.03
Cholesterol	0.03	0.01	0.05	0.02
Volatile acids	0.34	0.14	0.31	0.11
Ether-insoluble				
Uric acid	0.33	0.13	0.34	0.12
Creatine-creatinine	0.20	0.08	0.17	0.06
Amino acids	9.05	3.71	9.01	3.16
Hexoses	9.77	4.00	8.65	3.03
Pentoses	0.77	0.31	0.66	0.23
Sum	68.74	28.15	85.29	29.91
Volatile solids	72.19	29.60	87.86	30.81

*Constituent concentration in original sewage.
†As percent of soluble fraction total solids.
‡Corrected for detergent and phenol content.
§Corrected for cholesterol content.

2. Hunter, 1959

CONTRIBUTION OF THE ALCOHOL, ETHER-SOLUBLE MATTER
(TOTAL GREASE) TO WHOLE SEWAGE

Organic Constituent	Winter-Spring, 1959			Fall-Winter, 1959-60		
	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)	Settleable Fraction (mg/l)	Supracolloidal Fraction (mg/l)	Colloidal Fraction (mg/l)
Free fatty acids						
Unsaturated	0.18	0.24	0.20	0.17	0.21	0.11
Saturated	0.71	1.40	1.28	0.97	1.45	1.71
Phenols	0.004	0.002	0.002	0.005	0.001	0.001
Detergents	0.08	0.14	0.10	0.11	0.13	0.09
Glyceride fatty acids						
Unsaturated	1.13	0.88	0.24	0.94	0.71	0.25
Saturated	5.33	3.60	1.48	5.48	3.40	1.41
Phospholipids	0.00	0.02	0.04	0.00	0.02	0.03
Unsaponifiables	2.99	2.16	1.86	2.57	1.53	1.88
Sum	10.424	8.442	5.202	10.245	7.451	5.48
Total grease	11.70	9.57	5.55	11.25	8.65	6.06

3. Heukelekian, 1956

CONCENTRATION OF MINERAL CONSTITUENTS OF SEWAGE FRACTIONS

Element	Sewage Fractions (ppm in raw sewage)				Sum of Fractions
	Settleable	Supracolloidal	Colloidal	Dissolved	
Cl	--	--	--	20.0	20.1
Si	3.33	0.416	0.11	0.07	3.93
Fe	0.348	0.105	0.168	0.149	0.770
Al	0.075	0.035	0.015	0.007	0.132
Ca	0.512	0.300	0.857	8.15	9.82
Mg	0.415	0.24	0.19	9.46	10.31
K	0.20	0.19	0.10	5.43	5.92
Na	0.18	0.10	0.16	22.8	23.2
Mn	0.12	0.007	0.015	0.33	0.47
Cu	0.113	0.037	0.082	1.33	1.56
Zn	0.086	0.059	0.214	<0.04	0.359
Pb	0.30	0.067	0.11	<0.05	0.48
S	0.046	0.12	0.18	10.0	10.3
P	0.55	0.99	0.57	4.45	6.56
Sum of elements	6.28	2.67	2.77	82.3	93.8
Mineral weight*	6.61	2.77	2.78	83.2	95.3
Recovery (percent)†	95.1	96.3	99.9	99.0	--

*Fixed solids by a separate determination and calculated in terms of the total elemental content.

†Calculated from the sum of individual determinations and separate total fixed solids determinations.

4. Painter, 1958

CONCENTRATION OF SOME INORGANIC CONSTITUENTS IN
TWO 24 HOUR COMPOSITE SAMPLES OF SETTLED DOMESTIC SEWAGE

Constituent	Concentration (p.p.m.)	
	1st-2nd October 1956	30th April - 1st May 1957
Chloride	68	85
Sodium	--	100
Potassium	--	20
Calcium	109	109
Magnesium	3.5	6.5
Iron	2.1	0.8
Copper	0.55	0.2
Nickel	--	0.06
Zinc	0.75	0.65
Chromium	--	0.18
Manganese	--	0.05
Cadmium	--	nil
Lead	--	0.08

5. Vallentyne, 1957

SESTON (freshwater and marine)

Free: aphanicin, aphanin (=myxoxanthin), arginine, biotin(?). β-carotene, choline, cystine, flavacin, fructose, glucose, hentriacontane (?), histidine, lysine, maltose, monomethylamine, niacin, sucrose, thiamin, trimethylamine, tryptophan, tyrosine, vitamin A, vitamins D, vitamins B_{12}.

In hydrolysates:

Sugars: galactose, glucose, rhamnose, xylose.
Amino acids: α-alanine, arginine, aspartic acid, glutamic acid, glycine, histidine, hydroxyproline, leucine, phenylalanine, proline, tryptophan, tyrosine, valine.
Other compounds: aphanizophyll (=myxoxanthophyll?), astacene, cetyl alcohol, cholesterol (?), glucuronic acid, glycerol, lutein, peridinin.

DISSOLVED ORGANIC MATTER (freshwater and marine)

Free: biotin, dehydroascorbic acid, glucose, niacin (?), sucrose, thiamin, vitamins B_{12}.

In hydrolysates: α-alanine, aspartic acid, cystine, glutamic acid, glycine, histidine, tryptophan, tryosine.

AQUATIC SEDIMENTS (freshwater and marine)

Free:

Sugars: arabinose, fructose, fucose, galactose, glucose, maltose, ribose, sucrose, xylose.
Amino acids: α-alanine, glutamic acid.
Carotenoids: α-carotene, β-carotene, flavorhodin (?), leprotene (?), myxoxanthin (?), rhodopurpurin (?), rhodoviolascin, torulene (?).
Other compounds: acetic acid, biotin, n-butyric acid, cellulose, formic acid, pentatriacontane, β-sitosterol, thiamin (?), trimethylamine, tritriacontane, vitamins B_{12}.

In hydrolysates:

Sugars: arabinose, fructose (?), fucose, galactose, glucose, mannose, rhamnose, ribose, xylose.
Amino acids: α-alanine, arginine, aspartic acid, cystine, glutamic acid, glycine, histidine, isoleucine, leucine, lysine, serine, tryosine, valine.
Carotenoids: antheraxanthin (?), fucoxanthin (?), petaloxanthin (?), sulcatoxanthin (?), zeaxanthin (?).

5. Vallentyne, 1957 (Cont.)

In hydrolysates (cont.):
Other compounds: adenine, arachidic acid, behenic acid, caproic acid, caprylic acid, cerotic acid, cytosine, galacturonic acid, guanine, heptacosanoic acid, heptacosanol, heptoic acid, montanic acid, uracil.

SEWAGE AND ACTIVATED SLUDGE

Free: acetic acid, biotin, n-butyric acid, folic acid (?), indole (?), niacin (?), pantothenic acid (?), propionic acid, pyridoxine (?), riboflavin (?), skatole (?), thiamin, tryptophan, tyrosine, n-valeric acid (?), vitamins B_{12}.

TERRESTRIAL SOILS

Free:
Sugars: no free sugars identified.
Amino acids: α-alanine, γ-aminobutyric acid, arginine, asparagine, aspartic acid, glutamic acid, glutamine, glutamine, glycine, leucine and/or isoleucine, lysine, serine, threonine, valine.
Other acids: acetic acid, acrylic acid, p-aminobenzoic acid, 3,5-cresotic acid, α-crotonic acid, cyanuric acid, 8,9-dihydroxystearic acid, formic acid, α-hydroxystearic acid, lignoceric acid, oxalic acid, α-picoline-γ-carboxylic acid, sa

6. Murtaugh, 1965

LOWER FATTY ACIDS IN PRIMARY EFFLUENTS

Sample Source	Total Organic Acids (µe/l)	Individual Acids								Portion of Organic Acids* (%)
		Formic (µg/l)	Acetic (µg/l)	Propionic (µg/l)	Isobutyric (µg/l)	Butyric (µg/l)	Isovaleric (µg/l)	Valeric (µg/l)	Caproic (µg/l)	
PLANT A	460	587	12,000	3,550	428	1,540	541	379	135	64
	530	105	8,350	3,800	370	647	294	180	321	40
PLANT B	463	155	7,500	1,500	209	260	174	77	61	34
	163	46	1,700	237	114	112	122	24	16	23
PLANT C	161	148	145	16	12	23	125	4.7	15	4.7
	240	106	605	54	12	17	84	3.7	36	6.0

*Based on µe/l.

6. Murtaugh, 1965

LOWER FATTY ACIDS IN SECONDARY EFFLUENTS

Sample Source	Total Organic Acids (µe/l)	Individual Acids								Portion of Organic Acids* (%)
		Formic (µg/l)	Acetic (µg/l)	Propionic (µg/l)	Isobutyric (µg/l)	Butyric (µg/l)	Isovaleric (µg/l)	Valeric (µg/l)	Caproic (µg/l)	
PLANT A	81	127	187	68	143	112	524	20	--	19
	101	66	156	30	90	69	120	40	420	11
	99	144	172	8.6	51	111	195	16	--	10
	96	85	243	22	5.7	38	76	5.3	26	8.2
	84	124	192	10	29	39	102	14	18	10
PLANT B	71	58	122	15	8.3	11	14	2.5	11	5.7
	99	77	100	6.6	2.8	4.4	3.0	0.8	14	3.8
	115	87	115	6.5	3.8	5.4	3.5	1.8	28	3.7
PLANT C	90	51	25	1.2	4.2	2.6	4.0	0.8	9.6	1.9
	90	147	105	1.8	3.9	1.3	1.8	0.8	23	5.8
	75	89	157	5.1	0.2	1.6	1.3	0.6	28	6.6
PLANT D	79	66	68	2.4	0.9	1.3	0.8	0.7	30	3.7
	102	68	51	1.6	1.3	1.9	1.1	1.4	15	2.4

*Based on µe/l.

6. Murtaugh, 1965

LOWER FATTY ACIDS IN RIVER WATER

Sample Source*	Total Organic Acids (µe/l)	Individual Acids								Portion of Organic Acids† (%)
		Formic (µg/l)	Acetic (µg/l)	Propionic (µg/l)	Isobutyric (µg/l)	Butyric (µg/l)	Isovaleric (µg/l)	Valeric (µg/l)	Caproic (µg/l)	
Ohio, up	34.9	24	72	0.1	0.2	0.2	0.2	0.2	3.2	5.1
Ohio, up	13.0	39	15	0.4	0.2	0.2	0.3	0.1	0.8	8.6
Ohio, down	14.8	31	13	0.4	0.3	0.2	0.3	0.1	2.0	6.1
Ohio, up	31.1	12	13	0.7	0.3	0.2	0.2	0.3	6.2	2.2
Ohio, down	28.7	17	13	0.3	0.2	0.1	0.1	0.1	0.3	1.8
Little Miami, up	25.2	10	12	0.4	0.2	0.2	0.2	0.1	0.3	1.7
Little Miami, down	18.4	11	6	0.5	1.3	0.4	1.7	0.2	0.9	2.1
Tanners Creek	22.3	19	25	0.8	0.5	0.3	0.2	0.3	1.7	4.0

*Up and down refer to upstream and downstream from a municipality.

†Based on µe/l.

7. Teletzke, 1967

AMINO ACIDS FOUND IN RAW AND OXIDIZED SLUDGES

Amino Acids	Raw (mg/l total aa N)	Concentration in Sludge Oxidized at Given Temperature							
		175°C		200°C		225°C		250°C	
		Free* aa (mg/l)	Total** aa (mg/l)	Free aa (mg/l)	Total aa (mg/l)	Free aa (mg/l)	Total aa (mg/l)	Free aa (mg/l)	Total aa (mg/l)
Aspartic	97.6	9.5	44.7	1.5	5.1	Trace	1.8	None	None
Glutamic	250.0	82.8	254.8	56.8	78.2	9.0	15.3	None	None
Serine	87.5	8.3	47.7	Trace	Trace	None	None	None	None
Glycine	112.0	47.0	108.8	14.0	32.0	4.3	10.3	3.3	3.2
Threonine	88.4	None	43.2	None	6.3	None	None	None	None
Alanine	277.0	97.3	206.2	31.0	46.7	2.6	6.8	None	None
β Alanine	None	20.5	30.6	23.6	28.2	25.0	30.0	10.0	10.5
Arginine	90.5	None	None	None	None	None	None	None	None
Tyrosine	None	None	None	None	None	None	None	None	None
Histidine	None	None	None	None	None	None	None	None	None
Valine	85.2	5.9	58.8	2.8	11.8	1.2	1.8	None	None
Methionine	148.2	2.3	66.5	4.6	None	None	None	None	None
Isoleucine	51.6	9.8	57.3	7.9	9.6	None	None	None	None
Leucine	91.4	9.4	52.5	5.1	7.1	None	None	None	None
Proline	40.8	6.1	40.2	Trace	Trace	None	None	None	None
γ Amino butyric	None	5.4	14.6	8.4	17.1	5.0	10.8	1.2	7.3
Unknown	11.5	2.5	13.9	2.7	4.3	1.6	2.0	None	None
Total	1,432	307	1,040	158	246	49	79	14.5	21

*Free aa = free amino acid as determined on the unaltered sample.

**Total aa = total amino acid as determined on samples subjected to hydrochloric acid hydrolysis.

B. Clark, 1969

SURFACE H_2O (nM FAA/l)**

Site	La Jolla	Bird R. Kelp	Ab. Cove	V. Pt.	V. Pt.†	V. Pt.
Sample No.	11	12	5	7	15	18
Date	10 X 68	10 X 68	26 IX 68	26 IX 68	20 IX 68	5 XII 68
Depth						
Cys	-	7.4	-	-	-	-
Arg	20.7	24.7	92.9	72.7	30.1	59.1
Gly	88.8	78.5	64.5	188.9	44.2	77.4
Lys	18.7	33.7	30.7	39.9	22.4	39.9
His	21.9	37.2	28.8	62.0	11.6	41.2
Glu	153.2	141.3	50.8	27.9	34.4	36.3
Asp	77.1	83.8	141.3	82.0	6.0	84.1
Gly	168.2	188.0	155.5	425.7	153.8	222.7
Ser	133.2	213.6	186.1	250.2	94.6	213.2
Ala	43.5	65.1	106.1	61.7	45.3	112.9
Tyr	6.9	19.0	23.2	17.4	12.3	25.1
Met*	-	1.9	-	3.7	-	8.2
Val	21.9	19.3	33.8	33.9	12.3	29.2
Phe	62.6	38.2	40.9	65.8	17.7	48.5
Phe	31.2	9.6	2.7	11.4	12.9	17.1
Iso	4.8	17.0	18.4	18.7	5.9	16.9
Leu	20.6	9.1	27.4	19.5	11.3	17.1
Prop	26.8	20.5	16.6	21.5	21.6	57.1
Yellow III	-	-	-	-	-	-
Yellow 2	-	-	-	-	2.2	-
Yellow 11	-	-	-	-	-	-
a-A	-	1.8	-	3.3	-	0.9
a-B	-	-	0.7	13.9	2.2	10.0
TOTAL	900.1	1010.5	1021.4	1336.6	538.7	1134.5

*Tentatively estimated by visual comparison with standard chromatogram
†Water very turbid; heavy surge and surf
*Includes methionine-sulfoxide
**nM FAA/l = nano moles free amino acid per liter.

B. Clark, 1969

BOTTOM H_2O (nM FAA/l)

Site	La Jolla	La Jolla	Ab. Cove	A. Cove	Ab. Cove	V. Pt.	V. Pt.	V. Pt.	V. Pt.†	V. Pt.†	V. Pt.
Sample No.	9	10	1	2	6	3	4	8	13	14	17
Date	10 X 68	10 X 68	5 IX 68	5 IX 68	26 IX 68	5 IX 58	5 IX 68†	26 IX 68	20 XI 68	20 XI 68	5 XII 68
Depth	40'	40'	30'	30'	30'	30'	30'	30'	30'	15'	30'
Cys	-	-	-	-	-	-	-	-	-	-	-
Arg	49.7	24.5		70.0	106.3	152.5	41.8	65.6	101.1	8.2	76.5
Gly	150.9	129.8	985.5	956.0	355.9	279.8	485.8	116.4	200.5	49.2	144.3
Lys	22.4	56.9	57.0	20.5	140.8	120.2		74.9	91.1	16.9	158.0
His	66.1	50.1	198.9	126.1	71.9	86.0	149.8	94.5	137.8	13.1	96.7
Glu	54.4	32.6	83.3	64.5	57.6	86.1	102.7	57.5	76.2	22.8	52.2
Asp	95.1	73.4	328.8	137.5	170.8	228.9	537.7	162.3	241.3	44.3	247.2
Gly	358.9	477.6	284.9	66.9	569.4	269.0	389.1	645.0	493.2	156.2	414.2
Ser	365.6	378.0	537.5	204.4	601.8	332.0	566.7	321.8	522.3	115.9	305.5
Ala	116.8	120.7	353.3	178.0	291.9	186.2	168.3	147.2	223.1	58.7	195.5
Tyr	25.0	36.8	91.3	69.4	104.6	61.6	33.1	47.2	55.0	39.5	73.6
Met*	12.0	3.4	67.3	-	26.5	7.3	-	16.6	73.0	-	16.2
Val	36.6	34.8	158.8	101.0	103.9	62.5	56.7	35.7	85.5	21.8	60.8
Phe	90.3	87.4	243.9	119.5	177.5	89.0	161.1	96.3	98.3	86.5	102.8
Phe	2.1	29.8	77.6	8.4	-	-	-	-	-	-	-
Iso	14.1	23.5	87.5	48.0	33.9	36.4	6.3	20.8	50.4	18.7	87.1
Leu	14.1	28.3	106.1	63.8	59.6	53.3	65.8	21.5	47.4	10.6	32.7
Prop	30.9	39.8	65.2	116.1	73.3	63.2	76.4	25.3	45.7	10.3	41.6
Yellow III	-	-	-	-	71.5	41.2	107.0	55.4	60.0	52.9	34.1
Yellow 2	-	-	-	-	-	-	-	-	-	-	-
Yellow 11	-	-	-	-	-	-	-	-	-	-	-
a-A	-	-	-	-	-	-	-	-	-	-	-
a-B	10.6	30.5	8.9	31.8	-	-	-	-	-	-	3.7
TOTAL	8.4	27.4	-	-	29.3	10.5	9.0	2.1	-	-	
	1487.9	1648.7	3681.9	2384.4	3298.4	2086.0	2976.3	1977.9	2743.8	781.4	2587.8

†Water very turbid; heavy surge and surf

B. Clark, 1969

INTERSTITIAL H_2O (nM FAA/l)

Site	V. Pt.	V. Pt.	V. Pt.
Sample No.	16	19	20
Date	5 XII 68	13 I 69	13 I 69
Depth	30'	23'	18'
Cys	-	-	-
Arg	130.1	113.4	185.4
Gly	367.4	274.4	411.2
Lys	209.5	69.4	159.1
His	80.8	58.2	123.8
Glu	29.7	60.6	69.3
Asp	132.6	187.1	235.8
Gly	162.1	648.1	788.6
Ser	382.6	553.5	679.0
Ala	225.8	266.9	357.6
Tyr	69.1	52.2	86.4
Met*	-	13.9	22.4
Val	65.1	69.3	125.7
Phe	214.2	104.6	235.8
Phe	-	-	-
Iso	33.4	34.9	52.9
Leu	24.5	32.0	54.1
Prop	34.5	42.0	74.3
Yellow III	27.0	67.7	49.2
Yellow 2	-	12.9	13.9
Yellow 11	-	-	-
a-A	15.7	-	-
a-B	-	-	-
TOTAL	26.5	2.0	9.1
	2281.3	2679.0	4010.0

9. Hume, 1962

ORIGINAL HYPERION EFFLUENT AND SEA WATER CHARACTERISTICS

Component	To Sept. 1957		
	Characteristics Sea Water Cl = 18.55% (mg/l)	1-Mile Outfall 265 mgd -- High Rate Activated Sludge Effluent and Elutriation Overflow	
		mg/l	lb/day
Hardness (as $CaCO_3$)	--	212	469,000
Alkalinity (as $CaCO_3$)	--	272	602,000
Ca	389	50	111,000
Mg	1,262	23	51,000
Na	10,293	214	473,000
K	376	16	35,000
SO_4	2,597	148	327,000
Cl	18,550	234	518,000
Al	0-.02	0.04	88
As	0.003-0.03	0.01	22
Cd	0.00003-0.00001	0.05	110
Cr (hexavelent)	--	0.10	220
Cu	0.001-0.025	0.20	440
Fe	0.001-0.06	1.3	2,880
Mn	0.001-0.01	0.04	88
Ni	0.0001-0.006	0.35	770
Pb	0.003-0.005	0.08	180
Zn	0.008-0.021	0.35	770

9. Hume, 1962 (Cont.)

ORIGINAL HYPERION EFFLUENT AND SEA WATER CHARACTERISTICS

Component	To Sept. 1957		
	Characteristics Sea Water Cl = 18.55% (mg/l)	1-Mile Outfall 265 mgd -- High Rate Activated Sludge Effluent and Elutriation Overflow	
		mg/l	lb/day
B	5-25	1.0	2,210
F	1.3-1.4	1.5	3,320
SiO_2	0.01-6	20	44,000
Suspended solids	--	165	365,000
Volatile SS	--	100	220,000
BOD	--	80	177,000
Oil and grease	--	1-10	2,210-22,100
Detergent (ABS)	0	7-8	15,500-17,700
Phenol	--	0.02	44
Cyanide	--	0.09	200
Sulfide (dissolved)	--	0.0-0.1	0-220
Total nitrogen	0.03-0.9	40-50	88,500-111,000
Phosphate-phosphorus	0.001-0.06	8	17,700
Vitamin B_{12}	2×10^{-7}-20×10^{-7}	5×10^{-3}	11.06

9. Hume, 1962

FUTURE HYPERION EFFLUENT CHARACTERISTICS

Component	Future (1960)					
	1-Mile Outfall, 120 mgd Standard Rate Activated Sludge Effluent		7-Mile Outfall, 5 mgd Digested Sludge		5-Mile Outfall, 140 mgd Primary Effluent	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
Hardness	212	212,000	212	9,000	212	248,000
Alkalinity	272	272,000	272	12,000	272	318,000
Ca	50	50,000	50	3,000	50	58,000
Mg	23	23,000	23	1,000	23	27,000
Na	214	214,000	214	9,000	214	250,000
K	16	16,000	16	300	16	18,700
SO_4	148	148,000	148	6,000	148	173,000
Cl	234	234,000	234	10,000	234	274,000
Al	0.04	40	0.04	1	0.04	47
As	0.01	10	0.01	<1	0.01	12
Cd	0.05	50	0.05	2	0.05	58
Cr (hexavalent)	0.10	100	0.10	3	0.10	117
Cu	0.20	200	0.20	6	0.20	234
Fe	1.3	1,300	1.3	60	1.3	1,520
Mn	0.04	40	0.04	1	0.04	47
Ni	0.35	350	0.35	10	0.35	410
Pb	0.08	80	0.08	6	0.08	94
Zn	0.35	350	0.35	10	0.35	410

9. Hume, 1962 (Cont.)

FUTURE HYPERION EFFLUENT CHARACTERISTICS

Component	Future (1960)					
	1-Mile Outfall, 120 mgd Standard Rate Activated Sludge Effluent		7-Mile Outfall, 5 mgd Digested Sludge		5-Mile Outfall, 140 mgd Primary Effluent	
	mg/l	lb/day	mg/l	lb/day	mg/l	lb/day
B	1.0	1,000	1.0	40	1.0	1,170
F	1.5	1,500	1.5	60	1.5	1,760
SiO_2	20	20,000	20	600	20	23,400
Suspended solids	25	25,000	7,000	367,000	225	263,000
Volatile solids	15	15,000	3,500	183,000	175	204,000
BOD	12	12,000	4,000	210,000	200	234,000
Oil & grease	1-5	1,000-5,000	-	-	10-20	11,700-23,400
Detergent	2-7	2,000-7,000	-	-	8-10	9,300-11,700
Phenol	<0.005	<5	-	-	0.03	35
Cyanide	0.08	80	-	-	0.10	117
Sulfide	0.0	0	-	-	0.5	584
Total nitrogen	40-50	40,000-50,000	175	7,300	40-50	46,700-58,400
Phosphate	8	8,000	245	10,200	8	9,300
Vitamin B_{12}	1×10^{-3}	1.00	150×10^{-3}	6.26	3×10^{-3}	3.51

10. Bargman and Parkhurst, 1969

Wastewater constituents discharged to the ocean from Hyperion (340 mgd) and Whites Point (360 mgd). Tributary population - 7 million. (For the year 1968)

Constituent	Tons/Day
Dissolved Solids	3,600
Chloride (Cl)*	1,150
Sodium (Na)*	880
Sulfate (SO_4)	610
Suspended Solids (including digested sludge)	565
BOD	560
Total Nitrogen (N)	165
Phosphate (PO_4)	100
Grease	90
Potassium (K)	82
Thiosulfate (S)	50
Detergents	21
Phenols	9
Iron (Fe)	7
Fluoride (F)	5
Boron (B)	4.4
Zinc (Zn)	2.4
Chromium, Total (CR)	1.3
Copper (Cu)	1.0

*Does not include individual direct discharges of oil field brine to ocean.

(Continued)

10. Bargman and Parkhurst, 1969 (Cont.)

Wastewater constituents discharged to the ocean from Hyperion (340 mgd) and Whites Point (360 mgd). Tributary population - 7 million. (For the year 1968)

Constituent	Pounds/Day
Nickel (Ni)	1,125
Cyanide (CN)	930
Lead (PB)	730
Manganese (Mn)	400
Cadmium (Cd)	270
Arsenic (As)	100
Selenium (SE)*	55
Hexavalent Chromium (CR^{+6})	30
Barium (BA)*	0
Silver (AG)*	0

*Determined for Los Angeles City only; not reported for County Sanitation Districts of Los Angeles County.

11. Thompson, 1964

SPECTROGRAPHIC ANALYSIS FOR METALS CONTENT OF AIR-DRIED SEWAGE SLUDGE
(As percent of air-dried sludge)

Elements	Nichols Hills[1]	Okla.City Northside No. 1[2]	Okla.City Northside No. 2[2]	Okla.City Southside[3]	Broken Bow[4]	Idabel[5]	Norman No. 1[6]	Norman No. 2[6]	Holdenville[7]	Hugo[1]	Lawton[1]	Enid[2]
MAJOR												
Aluminum	Major	Major	Major	Major	Major	Major	Major	Major	Minor	Major	Major	Major
Calcium	Major	Major	Major	Major	1.30	Major	Minor	3.00	1.00	Minor	Minor	Major
Iron	2.00	2.00	2.00	1.30	2.00	2.00	1.50	1.50	2.00	2.00	2.00	2.00
Magnesium	1.00	1.50	1.00	1.50	1.00	1.00	1.30	1.30	0.10	0.50	1.00	1.00
Silicon	Major	Major	Major	Minor	Major	Major	Major	Major	Minor	Major	Major	Major
Titanum	1.50-2.00	1.50-2.00	1.50-2.00	1.00-1.50	1.50-2.00	1.50-2.00	1.50-2.00	1.50-2.00	0.10	1.00-2.00	0.50	0.70
INTERMEDIATE												
Barium	0.30	0.30	0.30	0.30	0.30	0.50	0.70	0.10	0.01	0.10	0.10	0.50
Copper	0.50	0.30	0.30	0.60	0.10	0.08	0.20	0.20	0.10	0.10	0.10-0.20	0.30
Manganese	0.10+	0.10+	0.10+	0.10	0.07	0.09	0.10	0.10	0.01	0.10	0.05	0.10
Sodium	0.05	0.07	0.05	1.00	0.10	0.10	1.00	1.00	0.20	0.20	1.00	0.70
Nickel	0.08	0.05	0.05	0.30	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Tin	0.10	0.10	0.06	0.20	0.05	0.05	0.07	0.06	0.05	0.05	0.10	0.10
Vanadium	1.50	0.10	0.10	0.10	0.07	0.20	1.00	1.00	0.05	0.05	0.03	0.07
Zinc	0.30	0.50	0.50	0.70	0.50	0.70	0.70	0.70	0.50	0.50	0.30	0.30
Silver	0.01	0.01	0.01	0.10	0.01	0.01	0.01	0.01	0.05	0.05	0.01	0.03
Zirconium	0.05	0.05	0.05	0.05	1.00	1.00	0.50	0.10	0.01	0.01	0.03	0.05

(Continued)

11. Thompson, 1964 (Cont.)

SPECTROGRAPHIC ANALYSIS FOR METALS CONTENT OF AIR-DRIED SEWAGE SLUDGE
(As percent of air-dried sludge)

Elements	Nichols Hills[1]	Okla.City Northside No. 1[2]	Okla.City Northside No. 2[2]	Okla.City Southside[3]	Broken Bow[4]	Idabel[5]	Norman No. 1[6]	Norman No. 2[6]	Holdenville[7]	Hugo[1]	Lawton[1]	Enid[2]
TRACE												
Boron	0.01	0.01	0.01	0.007	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Beryllium	-	-	-	-	-	-	-	-	-	-	T	T
Chromfum	0.06	0.01	0.01	0.10	0.01	0.01	0.01	0.01	T	T	T	0.03
Cobalt	0.01	0.05	0.05	-	T	T	-	-	-	0.005	0.005	0.01
Gallium	0.01	0.01	0.01	T	0.005	0.005	0.005	01005	0.005	0.005	0.003	0.001
Molybdenum	0.007	0.007	0.005	±0.10	0.01	0.01	0.01	0.01	T	T	0.03	0.03
Yttrium	T	T	T	-	T	T	T	T	-	T	T	T
Ytterbium	T	T	T	-	-	-	-	-	-	-	-	T
ASH CONTENT (%)	45.70	49.30	54.50	47.00	76.00	66.00	59.00	64.00	65.20	63.20	43.01	54.90

[1]Primary settling, standard-rate trickling filter, final settling, separate sludge digestion.
[2]Primary settling, activated sludge, final settling, separate sludge digestion.
[3]Primary settling, two-stage filtration, final settling, separate sludge digestion.
[4]Clarigester, standard-rate high-rate trickling filter, final settling.
[5]Primary settling, standard-rate trickling filter, separate sludge digestion.
[6]Biosorption, final settling, separate sludge digestion.
[7]Imhoff tank, standard-rate fixed-nozzle filter, final settling.

12. Wilson, 1968

EFFLUENT AND RECHARGED EFFLUENT QUALITY

	Concentration in Effluent mg/l	Concentration in Recharged Effluent mg/l
Calcium	34	82
Magnesium	51	92
Sodium	200	220
Potassium	14	16
Bicarbonate	451	560
Chloride	177	255
Sulfate	160	220
Nitrate	18	72
pH	7.6	7.2
COD	115	0
BOD	100	0
Total Dissolved Solids	1,807	1,481

13. Turekian and Scott, 1967

River and State	Suspended Load mg/l	Parts per Million					
		Cr	Ag	Mo	Ni	Co	Mn
1. Brazos, Texas	954	100	0.4	11	30	20	690
2. Colorado, Texas	150	82	0.6	10	40	17	780
3. Red, Louisiana	436	37	0.3	5	6	7	320
4. Mississipi, Arkansas	185	150	0.7	18	100	33	2,300
5. Tombigbee, Alabama	25	220	1.0	22	200	31	5,900
6. Alabama, Alabama	54	150	4.0	19	100	34	3,700
7. Chattahoochie, Georgia	71	190	7.0	20	100	35	2,400
8. Flint, Georgia	12	210	1.0	28	100	39	5,100
9. Savannah, S. C.	30	460	2.0	35	250	36	4,400
10. Wateree, S. C.	37	200	1.5	24	100	34	7,000
11. Pee Dee, South Carolina	188	150	0.4	15	100	23	1,300
12. Cape Fear, North Carolina	61	130	0.7	16	70	21	1,700
13. Neuse, North Carolina	36	380	4.0	22	70	30	3,000
14. Roanoke, North Carolina	33	240	4.9	21	100	45	7,900
15. James, Virginia	41	290	7.0	29	300	60	15,000
16. Rappahannock, Virginia	28	140	1.0	31	80	46	2,200
17. Potomac, Virginia	34	170	1.5	23	400	94	7,700
18. Susquehamma, Pa.	54	290	15.0	32	>1000	>500	12,000

(Continued)

13. Turekian and Scott, 1967 (Cont.)

River and Country	Suspended Load mg/l	Parts per Million					
		Cr	Ag	Mo	Ni	Co	Mn
Rhone, France							
Avignon, June 1966	296	150	0.7	14	60	29	820
Rio Maipo, Chile							
Puente Alto, S. of Santiago, September 1966	41	68	1.0	44	40	76	2,400
Shales (Turekian and Wedepohl, 1961)		90	0.1	2.6	68	19	850

14. Neale, 1964

TAP WATER ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MAX	MIN
Organics, ppm:																									
BOD	0	-	-	-	-	-	-	-	-	-	-	-	-	6	0.5	-	-	-	-	-	1	-	2	6	0
COD	0	-	-	-	-	-	-	-	-	-	-	-	-	27	8	42	4	1.4	0	27	-	2	12	42	0
ABS	-	-	-	-	-	-	-	-	-	-	0	0	0.05	0.04	0.02	4.2	0.04	0.02	0.02	0.02	0	0.01	0.37	4.2	0
Cations, ppm:																									
Na^+	27	21	30	97	269	-	-	-	100	33	17	25	-	-	-	-	8	18	17	14	-	10	49	269	8
K^+	-	-	-	-	-	-	-	-	5	4	2	2	-	-	-	-	2	2	2	1.6	-	2	3	5	1.6
NH_4^+	0	-	-	0	0	0	-	0	-	2	0	0	[redacted]	-	-	-	0	0	0	0	-	0	0.1	2	0
Ca^{++}	39	28	56	29	17	37	45	-	87	22	58	53	17	-	-	13	20	22	12	108	-	96	42	108	12
Mg^{++}	37	1	17	7	3	Tr	25	-	29	16	7	8	4	-	-	35	5	11	11	30	-	21	16	37	0
Fe^{+++}	0.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Anions, ppm:																									
Cl^-	13	35	59	53	250	49	150	20	97	32	13	16	15	22	22	518	12	17	9	22	6	16	66	518	6
NO_3^-	9	-	-	-	-	9	22	0	5	2	4	9	-	0.5	0.1	3.0	0.1	6.2	5.3	0.37	-	2.7	5	9	0
NO_2^-	-	-	-	-	-	-	-	-	-	0.3	-	-	-	-	-	0.18	0.03	0.01	0.13	0.31	-	0.03	0.14	0.30	0.01
HCO_3^-	312	35	263	281	347	149	342	268	149	137	176	181	66	-	-	210	27	46	49	379	-	358	198	379	27
$CO_3^=$	0	10	0	0	0	0	0	-	0	-	0	0	0	-	-	5	1	0	0	0	-	-	0.1	10	0

Continued

14. Neale, 1964 (Cont.)

TAP WATER ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MAX	MIN
$SO_4^=$	34	19	21	8	0	58	75	19	291	17	44	47	12	-	-	84	56	79	56	96	-	53	56	291	0
$SiO_3^=$	71	13	30	35	35	-	-	-	11	-	-	-	8	-	-	-	-	-	-	-	-	-	29	71	11
$PO_4^{\equiv}$(Total)	0	2	0	0	3	0	0	0	-	2.5	0	0	0	0.5	3.5	3.8	0.04	0.05	0.03	0.02	-	-	8.1	3.8	0
$PO_4^{\equiv}$(Ortho)	0	0.5	0	0	1.5	0	0	0	-	-	0	0	0	-	-	3.3	0	0.01	0.01	0	-	-	0.3	3.3	0
Other:																									
Hardness (as $CaCO_3$) ppm	249	74	210	101	55	120	215	220	337	121	174	164	59	-	-	178	71	100	75	150	-	326	158	337	55
Alkalinity (as $CaCO_3$) ppm	255	45	210	230	284	122	280	220	122	112	144	148	54	-	-	180	24	38	40	311	-	294	164	311	24
Total dissolved solids, ppm	364	161	650	504	917	327	500	265	700	-	271	317	100	214	185	1130	98	177	140	520	155	344	382	917	98
pH	7.8	8.8	7.7	7.8	7.3	7.2	7.8	-	8.0	-	7.7	7.6	8.3	-	-	9.0	8.8	8.2	8.3	7.8	-	7.4	8.0	9.0	7.2

14. Neale, 1964

SECONDARY - EFFLUENT ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MIN	MAX
Organics, ppm																									
BOD	10	-	18	45	10	-	-	-	-	10	-	-	8	33	9	33	-	-	-	-	18	-	19	9	45
COD	-	-	-	-	-	-	-	-	-	-	-	-	-	135	44	158	163	99	79	49	-	78	101	44	163
ABS	-	-	-	-	-	-	-	-	-	-	6	9	-	2.9	2.4	10.0	10.1	7.2	6.3	4.6	7	9	6.8	2.4	10.1
Cations, ppm																									
Na^+	85	29	-	180	384	-	232	-	200	67	118	99	-	-	-	-	50	68	63	112	-	55	124	29	232
K^+	-	-	-	-	-	-	-	-	20	11	-	-	-	-	-	-	14	9	11	10	-	12	12	9	20
NH_4^+	22	-	-	15	3	5	-	8	44	8	-	-	-	-	-	36	9	21	29	25	-	0	17	0	44
Ca^{++}	96	78	62	45	42	40	58	-	97	33	68	60	-	-	-	-	64	53	54	109	-	97	66	33	109
Mg^{++}	12	16	23	16	17	Tr	26	-	30	17	13	16	-	-	-	-	14	20	22	33	-	22	19	Tr	30
Anions, ppm																									
Cl^-	85	55	121	90	450	165	260	173	197	69	143	79	137	77	64	532	52	67	49	124	90	62	143	52	532
NO_3^-	26	-	-	-	-	-	-	4	2	11	-	-	-	0.04	3.9	6.2	26	22	0.62	26	-	20	12	0.04	26
NO_2^-	-	-	-	-	-	-	-	-	-	2	-	-	-	-	-	0.62	2	0.3	0.26	1.1	-	1.8	1.5	0.26	2
HCO_3^-	303	209	-	420	385	110	298	293	398	200	219	403	146	-	-	327	212	243	314	428	-	409	296	110	428
$CO_3^=$	0	0	0	0	0	0	0	-	0	-	-	-	0	-	-	0	0	0	0	0	-	-	0	0	0

14. Neale, 1964 (Cont.)

SECONDARY - EFFLUENT ANALYSES

Reference	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V	AVG	MIN	MAX
$SO_4^{=}$	42	57	45	43	20	115	96	70	300	30	75	69	31	-	-	105	95	91	108	111	-	99	84	20	300
$SiO_3^{=}$	80	30	43	57	49	-	53	25	25	-	-	-	22	-	-	-	-	-	-	-	-	-	43	22	80
$PO_4^{=}$(Total)	41	9	37	33	25	50	29	12	-	10	35	43	21	8	5	29	35	19	20	18	-	29	25	5	50
$PO_4^{=}$(Ortho)	40	8	34	30	23	32	27	-	-	-	-	-	-	-	-	21.8	33.8	17.9	19	16.9	-	28	25	8	40
Other:																									
Hardness (as $CaCO_3$) ppm	290	259	250	175	175	153	250	230	366	153	224	213	100	-	-	-	218	215	227	411	-	332	235	100	411
Alkalinity (as $CaCO_3$) ppm	248	172	-	344	316	90	244	240	326	164	180	331	120	-	-	268	174	198	257	351	-	335	242	90	351
Total solids, ppm	727	477	844	872	1362	730	1041	540	1065	-	683	566	410	519	410	1302	472	525	597	648	480	492	703	410	1362
Suspended solids, ppm	-	-	-	-	-	-	-	-	-	-	-	-	18	-	-	-	-	-	-	-	-	-	-	-	-
pH	6.5	7.1	7.5	7.8	7.3	7.0	8.0	-	7.0	-	-	-	6.9	-	-	7.6	7.5	7.3	7.8	7.8	-	7.4	7.4	6.5	8.0

15. Bowen, 1966

ELEMENTARY COMPOSITION OF SOIL SOLUTIONS
AND
RIVER WATERS IN PPM[1]

Element	Soil Solution[2]		River Water[3]	
	Median	Range	Median	Range
Ag			0.00013	0.00001-0.0035
Al			0.24	0.01-2.5
Ar			0.6	
As			0.0004	<0.0004-0.23
Au			<0.00006	
B		0.03-10	0.013	0.01-1
Ba			0.054	0.009-0.15
Be			0.001	0.0001-0.001
Br		<0.001-0.01	0.021	0.005-140
C(HCO^-)	4	2-7	11	6-19
Ca	32	1-60(-1500)	15	4-120
Cd			0.08	
Cl	10	7-50(-8000)	7.8	5-35
Co			0.0009	<0.006
Cr			0.00018	0.0001-0.08
Cs			0.0002	0.00005-0.0002
Cu		0.01-0.06	0.01	0.0006-0.4

15. Bowen, 1966 (Cont.)

ELEMENTARY COMPOSITION OF SOIL SOLUTIONS
AND
RIVER WATERS IN PPM[1]

Element	Soil Solution[2]		River Water[3]	
	Median	Range	Median	Range
F			0.09	
Fe		0.1-0.25 (-25)	0.67	0.01-1.4
Ga			<0.001	
Hg			0.00008	
I		0.01	0.002	
K	3.5	1-11(-400)	2.3	1.4-10
Li			0.0011	0.00007-0.04
Mg	25	0.7-100 (-2400)	4.1	1.5-6
Mn		0.02-2 (-800)	0.012	0.00002-0.13
Mo		<0.001	0.000035	<0.007
N (NO_3^-)		2-800	0.23	0.01-08
Na	15	9-30(-3500)	6.3	3-25
Ni			0.01	0.0002-0.02
P	0.005	0.001-30	0.005	0.001-0.3(-12)
Pb			0.005	0.0006-0.12
Ra			3.9×10^{-10}	
Rb			0.0015	<0.008
Rn			1.7×10^{-15}	
S	5	<3-5000	3.7	0.9-30

15. Bowen, 1966 (Cont.)

ELEMENTARY COMPOSITION OF SOIL SOLUTIONS
AND
RIVER WATERS IN PPM[1]

Element	Soil Solution[2]		River Water[3]	
	Median	Range	Median	Range
Se		0.001-3	<0.02	
Si		0.5-12	6.5	2-12
Sn			0.00004	
Sr		<0.1	0.08	0.003-0.8
Th			0.00002	
Ti		≤0.07	0.0086	<0.11
U			0.001	0.00002-0.05
V			0.001	<0.007
Zn		0.1-0.3	0.01	0.0002-1
Zr			0.0026	0.00005-0.022

[1]Many elements vary in abundance in river water seasonally (e.g., Si) or even from day to day (e.g., Mn). Abnormal ranges are given in parentheses.

[2]Swaine (1955), Wiklander (1958), Vinogradov (1959), Fried and Shapiro (1961), Barber, et al. (1963), Bowen and Cawse (1965).

[3]Livingstone (1963a), Durrum and Haffty (1963).

15. Bowen, 1966

THE ELEMENTS IN SEA WATER[1]

Element	Chemical Form	ppm	Residence Time (years × 1000)	Percentage Retention
Ag	$AgCl_2$-	0.0003	2100	0.4
Al		0.01	0.1	0.00001
Ar	Ar	0.6		140
As	AsO_4H^{2-}	0.003		0.15
Au	$AuCl_4$-	0.000011	560	0.25
B	$B(OH)_3$	4.6		46
Ba	Ba^{++}	0.03	84	0.006
Be		0.0000006	0.15	0.00002
Bi		0.000017	45	0.01
Br	Br^-	65		2300
C	CO_3H^-, organic C	28		12
Ca	Ca^{2+}	400	8000	0.9
Cd	Cd^{2+}	0.00011	500	0.05
Ce		0.0004	6.1	0.0006
Cl	Cl^-	19000		13000
Co	Co^{2+}	0.00027	18	0.001
Cr		0.00005	0.35	0.00004
Cs	Cs^+	0.0005	40	0.04

15. Bowen, 1966 (Cont.)

THE ELEMENTS IN SEA WATER

Element	Chemical Form	ppm	Residence Time (years × 1000)	Percentage Retention
Cu	Cu^{2+}	0.003	50	0.005
F	F	1.3		0.2
Fe	$Fe(OH)_3$	0.01	0.14	0.000016
Ga		0.00003	1.4	0.0002
Ge	$Ge(OH)_4$	0.00007	7	0.004
H	H_2O	108000		6850
He	He	0.0000069	20000	0.05
Hf		<0.000008		<0.00024
Hg	$HgCl_4^{2-}$	0.00003	42	0.03
I	I^-, IO_3-?	0.06		1.1
In		<<0.02		
K	K+	380	11000	1.6
Kr	Kr	0.0025		130
La		0.000012	0.44	0.009
Li	Li+	0.18	20000	0.75
Mg	Mg^{2+}	1350	45000	5.1
Mn	Mn^{2+}	0.002	1.4	0.002
Mo	MoO_4^{2-}	0.01	500	0.6
N	Organic N, NO_3-, NH_4+	0.5	2.5	220

15. Bowen, 1966 (Cont.)

THE ELEMENTS IN SEA WATER

Element	Chemical Form	ppm	Residence Time (years × 1000)	Percentage Retention
Na	Na^+	10500	260000	40
Nb		0.00001	0.3	0.00004
Ne	Ne	0.00014		2
Ni	Ni^{2+}	0.0054	18	0.005
O	OH_2, O_2, SO_4^{2-}	857000		164
P	PO_4H^{2-}	0.07		0.006
Pa		2×10^{-9}		0.13
Pb	Pb^{2+}	0.00003	2	0.000002
Ra		6×10^{-11}		0.006
Rb	Rb^+	0.12	270	0.12
Rn	Rn	6×10^{-16}		0.1
S	SO_4^{2-}	885		300
Sb		0.00033	350	0.15
Sc		<0.000004	5.6	<0.00002
Se		0.00009		0.16
Si	$Si(OH)_4$	3	8	0.001
Sn		0.003	100	0.1
Sr	Sr^{9+}	8.1	19000	1.9

15. Bowen, 1966 (Cont.)

THE ELEMENTS IN SEA WATER

Elements	Chemical Form	ppm	Residence Time (Years × 1000)	Percentage Retention
Ta		<0.0000025		<0.0001
Th		0.00005	0.35	0.0005
Ti		0.001	0.16	0.00002
Tl	Tl^+	<0.00001		<0.002
U	$UO_2(CO_3)_3^{4-}$	0.003	500	0.1
V	$VO_5H_3^{2-}$	0.002	10	0.001
W	WO_4^{2-}	0.0001	1	0.006
Xe	Xe	0.000052		300
Y		0.0003	7.5	0.0008
Zn	Zn^{2+}	0.01	180	0.01
Zr		0.000022		0.000012

[1]Goldberg (1963), Goldberg (1965), Shutz and Turekian (1965)

16. Chow, 1968

SCOPE OF ISOTOPE-DILUTION ANALYSIS OF SEAWATER*

Class	Element	Isotope Pair†	Concentration in Seawater (μg/kg)	Method Used
I-a. Major constituents of seawater with unique isotope pairs	B	10 and 11	4.3×10^3	Volumetric
	C	12 and 13	2.8×10^4	Gasometric
	Mg	24 and 25	1.294×10^6	Volumetric
	Si	28 and 29	3.0×10^3	Colorimetric
	S	32 and 33	8.84×10^5	Gravimetric
	Cl	35 and 37	1.90×10^7	Volumetric
	K	39 and 41	3.90×10^5	Flame photometric
	Ca	42 and 43	4.24×10^5	Flame photometric
	Br	79 and 81	6.7×10^4	Volumetric
	Sr	86 and 88	8.1×10^3	Flame photometric Isotope dilution
I-b. Minor constituents of seawater with unique isotope pairs	Li	6 and 7	170	Isotope dilution
	Be	9 and 10	0.0006	Spectrographic
	Ti	47 and 49	1	Colorimetric
	Cr	52 and 53	2	Neutron activation
	Fe	56 and 57	8	Colorimetric
	Ni	60 and 61	5	Neutron activation
	Cu	63 and 65	3	Colorimetric
	Zn	66 and 67	5	Neutron activation
	Ga	69 and 71	0.03	Colorimetric
	Ge	72 and 73	0.06	Colorimetric

16. Chow, 1968 (Cont.)

SCOPE OF ISOTOPE-DILUTION ANALYSIS OF SEAWATER*

Class	Element	Isotope Pair	Concentration in Seawater (µg/kg)	Method Used
	Se	77 and 80	0.4	Colorimetric
	Zr	90 and 91	0.02	Fluorometric
	Mo	95 and 97	10	Colorimetric
	Ru	99 and 101	No data	-
	Ag	107 and 109	0.3	Neutron activation
	Sn	117 and 118	0.8	Neutron activation
	Te	125 and 128	No data	-
	Ba	135 and 138	50	Isotope dilution
	Nd	145 and 146	0.003	Neutron activation
	Sm	147 and 149	0.0005	Neutron activation
	Eu	151 and 153	0.0001	Neutron activation
	Gd	155 and 157	0.0007	Neutron activation
	Dy	161 and 163	0.0009	Neutron activation
	Er	166 and 167	0.0009	Neutron activation
	Yb	171 and 172	0.0008	Neutron activation
	Hf	178 and 179	<0.008	Neutron activation
	W	182 and 183	0.1	Colorimetric
	Os	188 and 189	No data	-
	Ir	191 and 193	No data	-
	Pt	194 and 195	No data	-

16. Chow, 1968 (Cont.)

SCOPE OF ISOTOPE-DILUTION ANALYSIS OF SEAWATER*

Class	Element	Isotope Pair†	Concentration in Seawater (µg/kg)	Method Used
	Hg	201 and 202	0.1	Colorimetric
	Tl	203 and 205	0.01	Spectrographic
	Pb	206 and 208	0.08	Isotope dilution
	Th	230 and 232	0.002	Alpha activity
	U	235 and 238	3	Isotope dilution
II. Minor constituents of seawater with suitable isotope pairs	V	50 and 51	2	Colorimetric
	Rb	85 and 87	120	Isotope dilution
	Pd	105 and 106	No data	-
	Cd	110 and 111	0.1	Colorimetric
	In	113 and 115	<20	Spectrographic
	Sb	121 and 123	0.3	Neutron activation
	I	127 and 129	64	Amperometric
	Cs	133 and 135	0.3	Flame photometric
	La	138 and 139	0.003	Neutron activation
	Ce	140 and 142	0.001	Neutron activation
	Lu	175 and 176	0.0002	Neutron activation
	Ta	180 and 181	<0.002	Neutron activation
	Re	185 and 187	No data	-

16. Chow, 1968 (Cont.)

SCOPE OF ISOTOPE-DILUTION ANALYSIS OF SEAWATER*

Class	Element	Isotope Pair†	Concentration in Seawater (μg/kg)	Method Used
III. Dissolved gases in seawater with unique isotope pairs	H	1 and 2	No data	-
	He	3 and 4	0.007	Isotope dilution
	N	14 and 15	1.55×10^4	Gasometric
	O	16 and 18	6.0×10^3	Volumetric
	Ne	20 and 21	0.120	Isotope dilution
	Ar	38 and 40	450	Isotope dilution
	Kr	84 and 86	0.210	Isotope dilution
	Xe	128 and 129	0.047	Isotope dilution
IV. Mono-isotopic elements in seawater	F	19	1300	Colorimetric
	Na	23	1.8×10^7	-
	Al	27	1	Fluorometric
	P	31	88	Colorimetric
	Sc	45	0.004	Neutron activation
	Mn	55	1.9	Neutron activation
	Co	59	0.4	Neutron activation
	As	75	2.6	Neutron activation
	Y	89	0.001	Neutron activation
	Nb (Cb)	93	0.02	Chromatographic

16. Chow, 1968 (Cont.)

SCOPE OF ISOTOPE-DILUTION ANALYSIS OF SEAWATER*

Class	Element	Isotope Pair†	Concentration in Seawater (µg/kg)	Method Used
	Rh	103	No data	-
	Pr	141	0.006	Neutron activation
	Tb	159	0.001	Neutron activation
	Ho	165	0.0002	Neutron activation
	Tm	169	0.0002	Neutron activation
	Au	197	0.01	Neutron activation
	Bi	209	0.02	Spectrographic

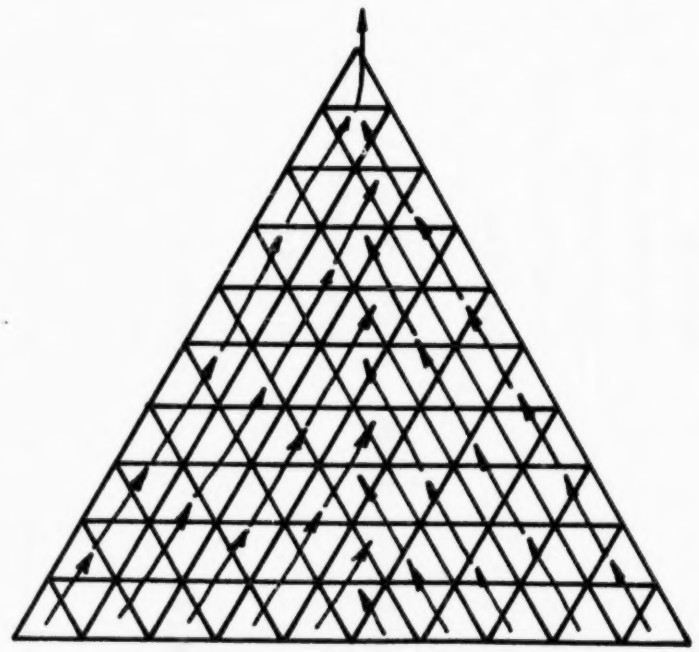
*For detailed information, see Goldberg, Riley and Skirrow

†Boldface denotes available tracers

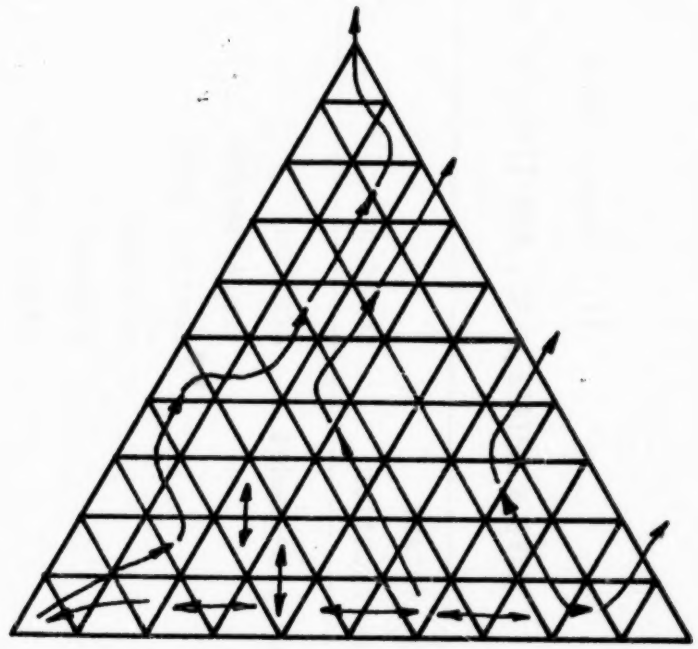
17. Young, 1968

OXYGEN UPTAKE, LAG, AND TIMES OF BACTERIAL PEAKS

O_2 Uptake Classification	Compound	Lag (Days)	Bacterial Peak (Days)
Readily degraded	Acetone	2	3
	Benzaldehyde	0	4
	Benzoic acid	0	2
	o-Cresol	1	3
	Ethanol	0	2
	Ethyl acetate	1	2
	Hydroquinone	1	3
	Maleic acid	1	2
	Methanol	1	2
	Methyl ethyl ketone	1	3
	Oxalic acid	0	2
Acclimation	Acrylonitrile	12	12
	Aniline	3	5
	Ethylene glycol	4	7
	Isopropanol	5	7
	Monoethanolamine	2	3
	Pyridine	9	2
Slightly oxidized	tert-Butanol	-	3
	Diethylene glycol	0	3
	Toluene	1	2
Control	Seed Blank	0	2
	Glucose-glutamic acid	0	2



NET OR WEB FEEDING SUCCESSION

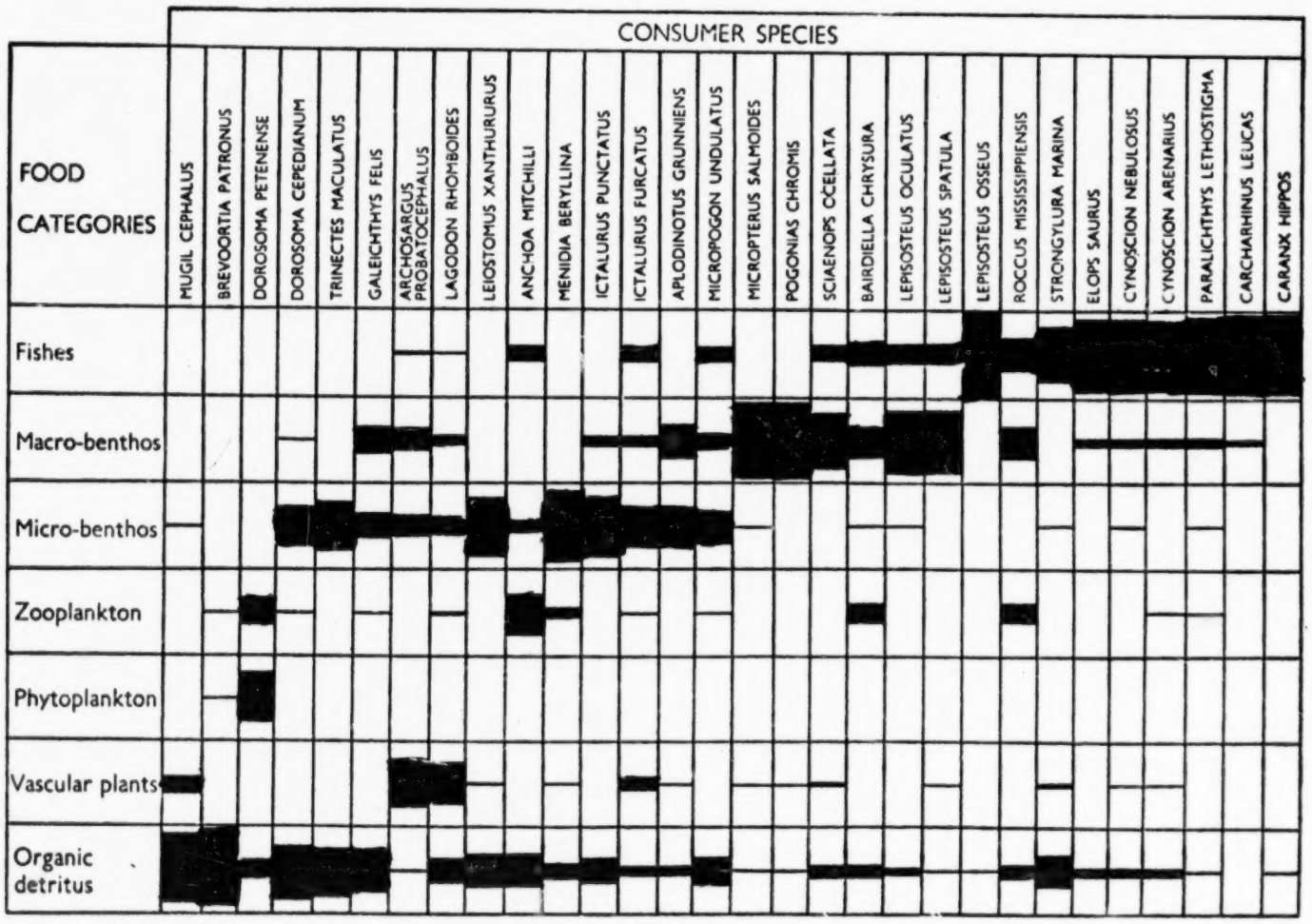


CHAIN FEEDING SUCCESSION

Figures 18 and 19: SCHEMATIC OF NET VERSUS CHAIN

20. Green (1968)

TROPHIC SPECTRUM OF THE FISH IN LAKE PONTCHARTRAIN, LOUISIANA
(after R. M. Darnell)



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